



# ***Macroscopic Arrays of Block Copolymers with Areal Densities of 10 Terbit/inch<sup>2</sup> and Beyond***

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Amherst, MA

\*Ulsan National Institute of Science and Technology

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Seagate Technologies

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University of California at Berkeley,  
Berkeley, CA

**Supported by: DOE BES, NSF MRSEC & CHM,  
Seagate Technologies**

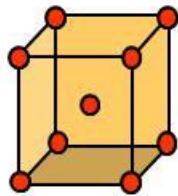
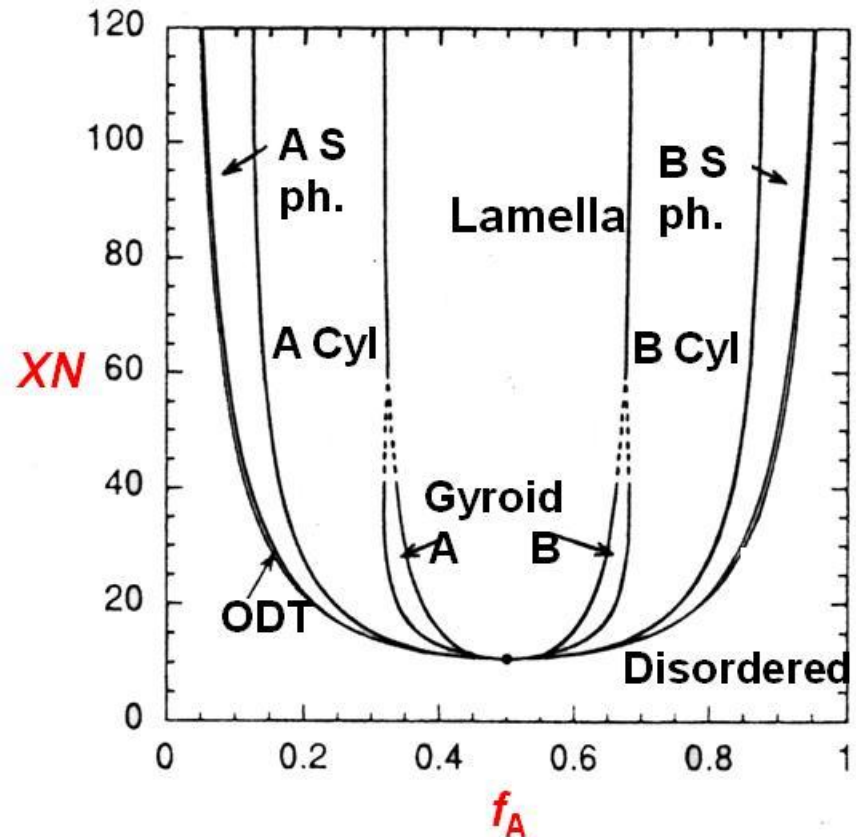
# Block Copolymers (BCPs) Morphology Diagram



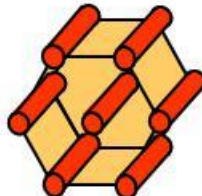
Block Volume Fraction,  $f$   
controls morphology

Flory Parameter,  $\chi$   
controls segregation

Degree of polymerization,  $N$   
controls domain size



S



C



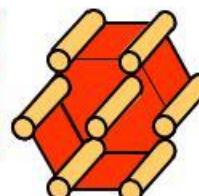
G



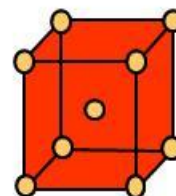
L



G'

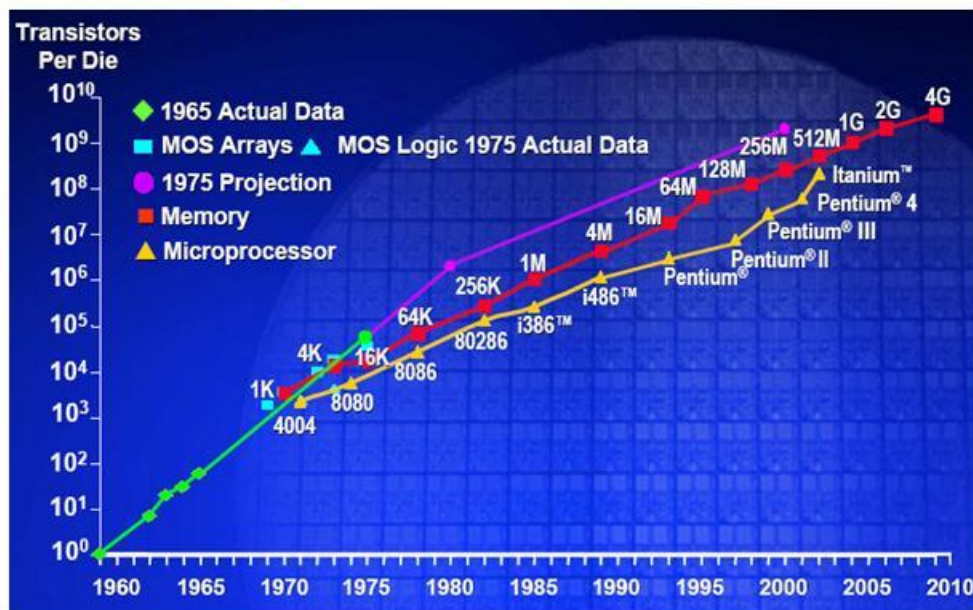


C'



S'

## Materials and processes for nanoscale devices



<http://www.intel.com/research/silicon/mooreslaw.htm>

### Relentless Reduction in Feature Size!

2004 = 90 nm      2007 = 65 nm      2010 = 45 nm

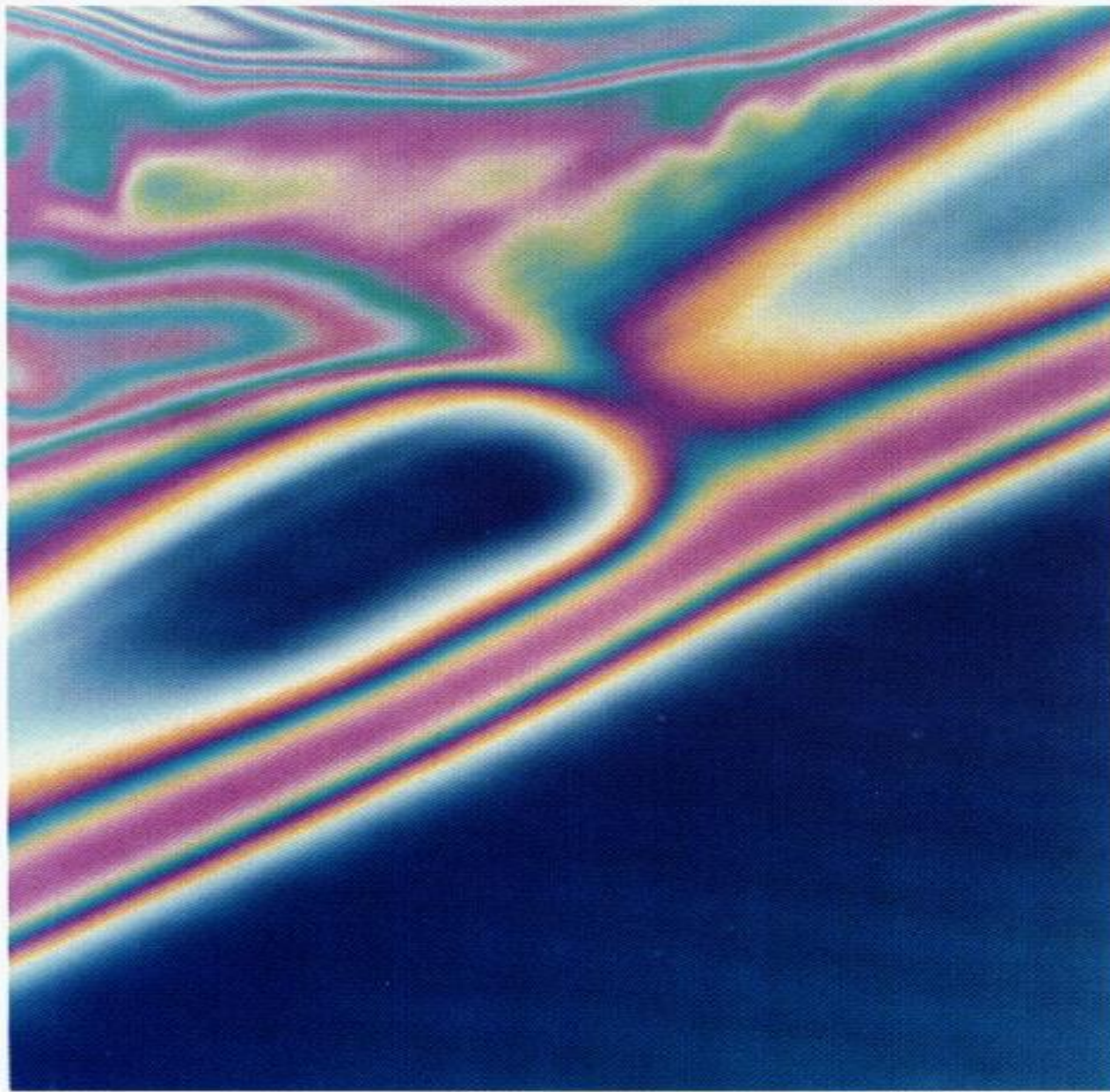
### Current top-down techniques

limitation of optical diffraction and the wavelength of light sources

### bottom-up approaches using self-assembly

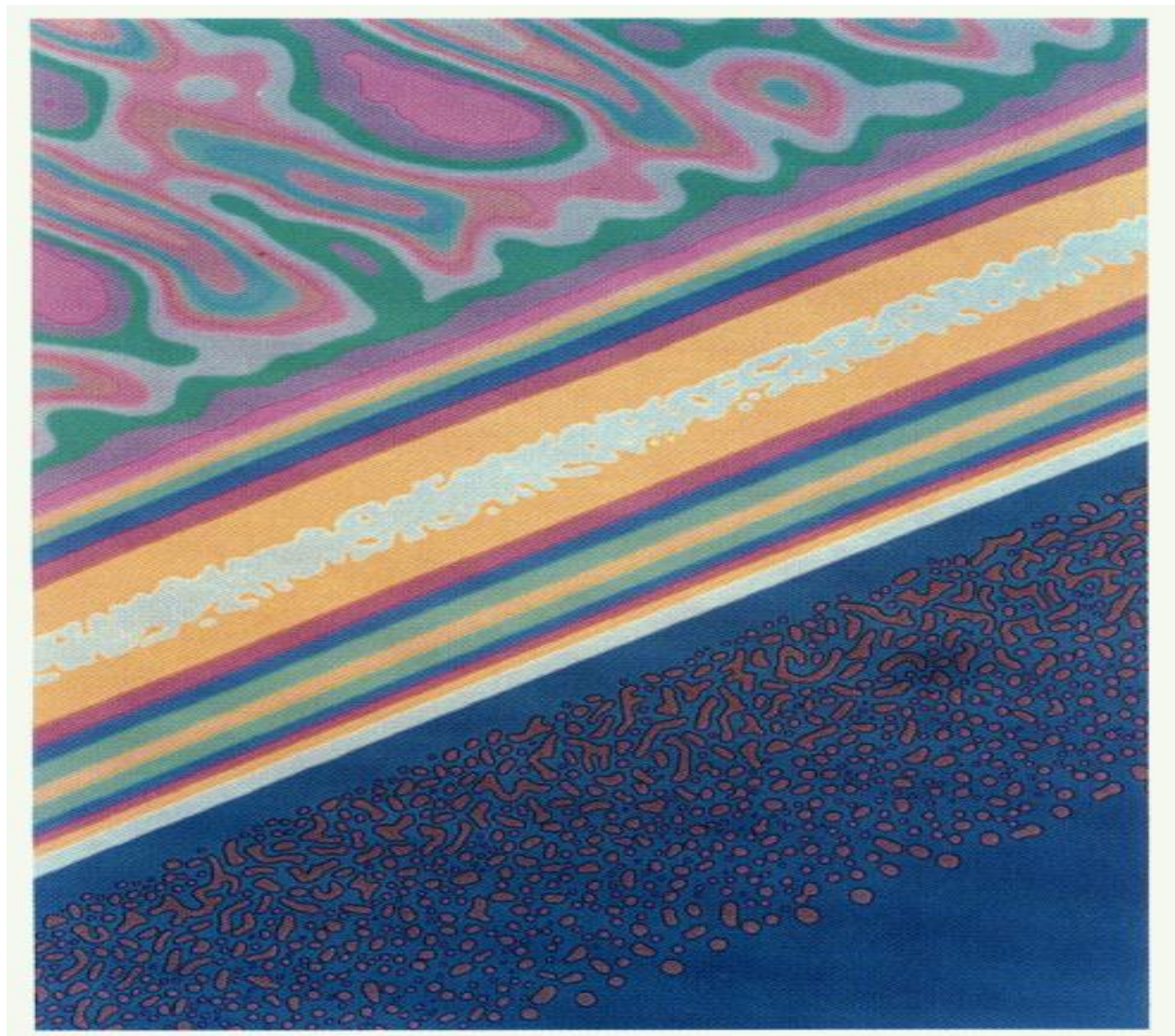
at length scales of 25 nm and below (ultra-small nanofabrication)



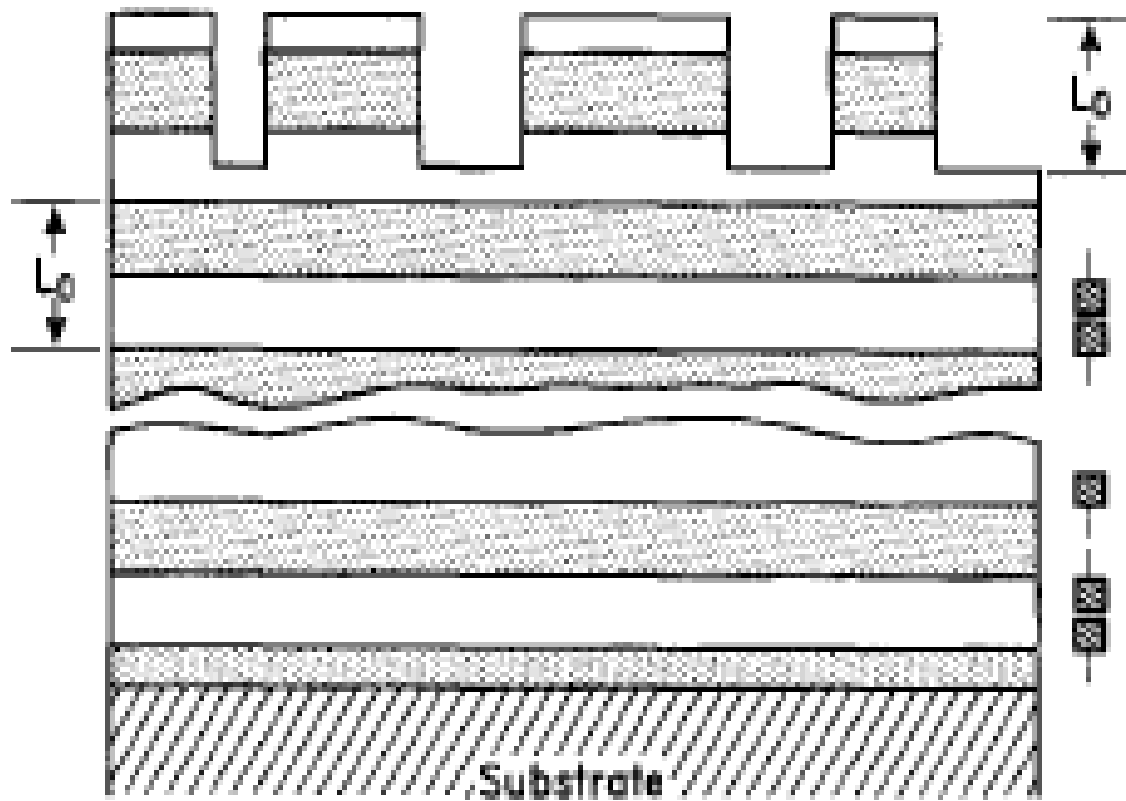


*Macromolecules* **1989**, 22, 2581–2589





*Macromolecules* 1989, 22, 2581–2589



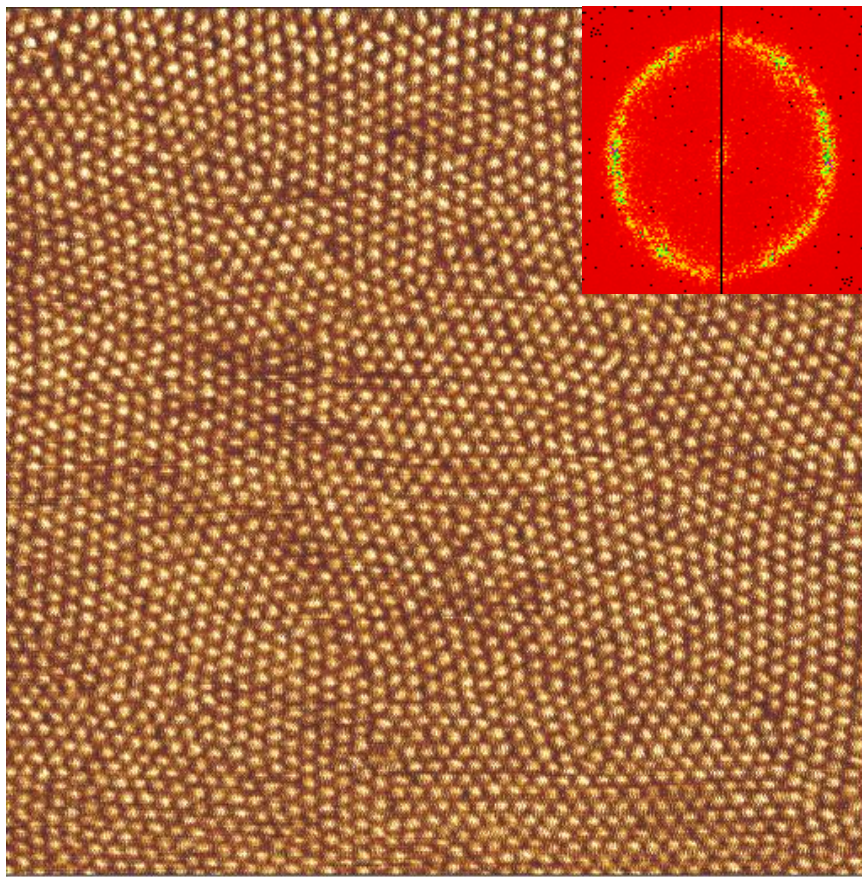
*Russell, T.P., Physica B, 1995, 213&214, 22.*





# *Balanced Interfacial Interactions*

*Thermal Annealing*



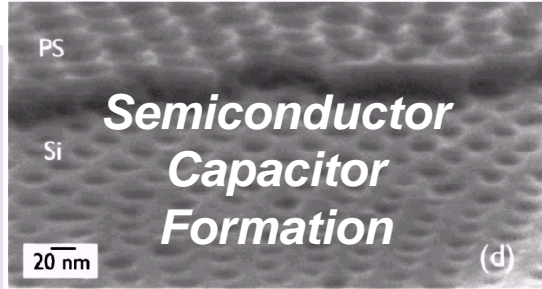
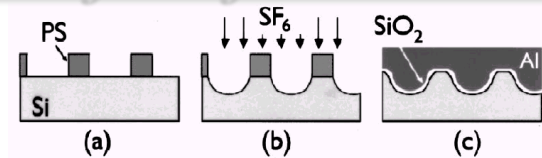
*UV Exposed*



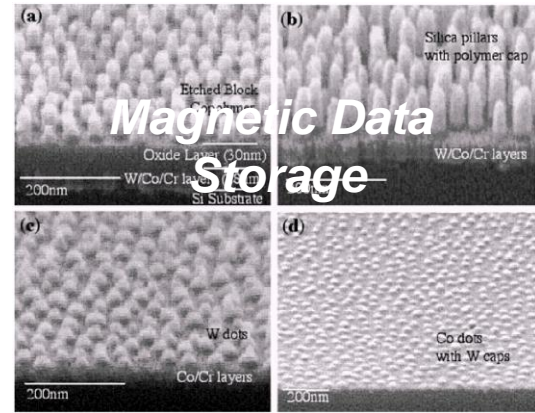




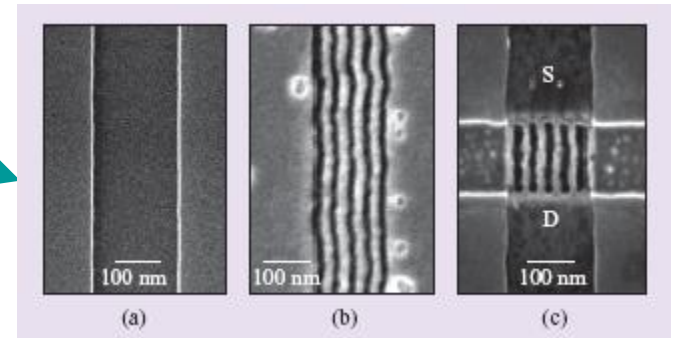
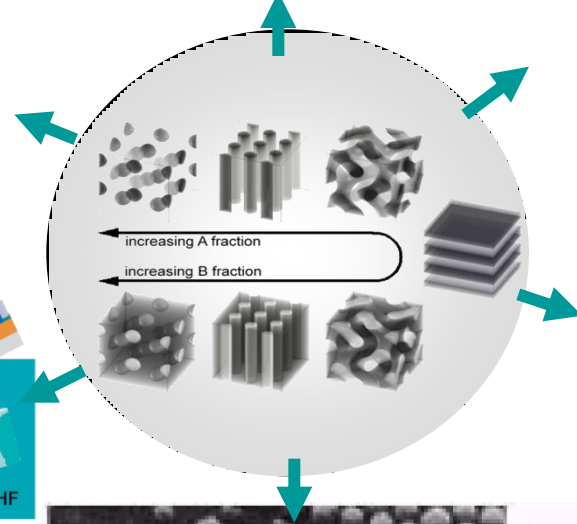
# Application of Self-Assembled Block Copolymers



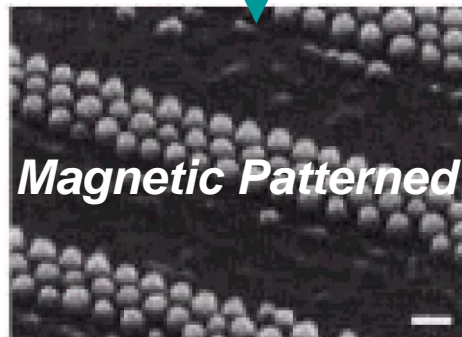
*Applied Physics Letters* **79** 409 (2001)



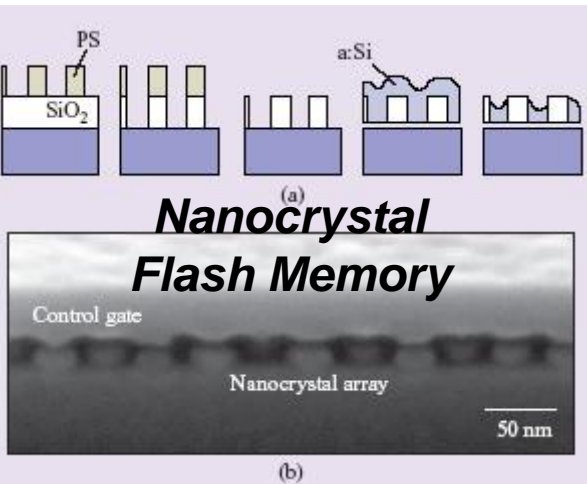
*Adv. Mater.* **13** 1174 (2001)



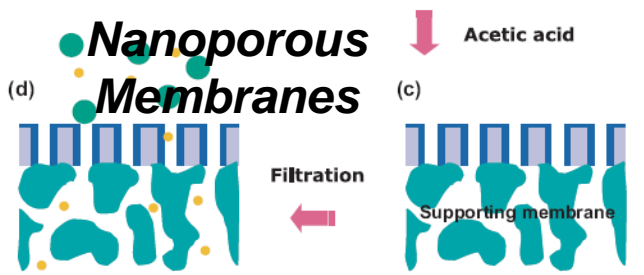
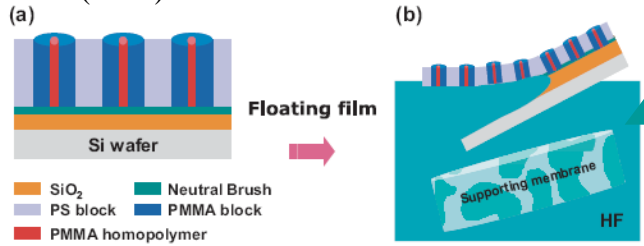
*Appl. Phys. Lett.* **87** 163116 (2005)



*IEEE Trans Magn* **38** 1949 (2002)



*IEEE International Electron Devices*  
16 (2007)



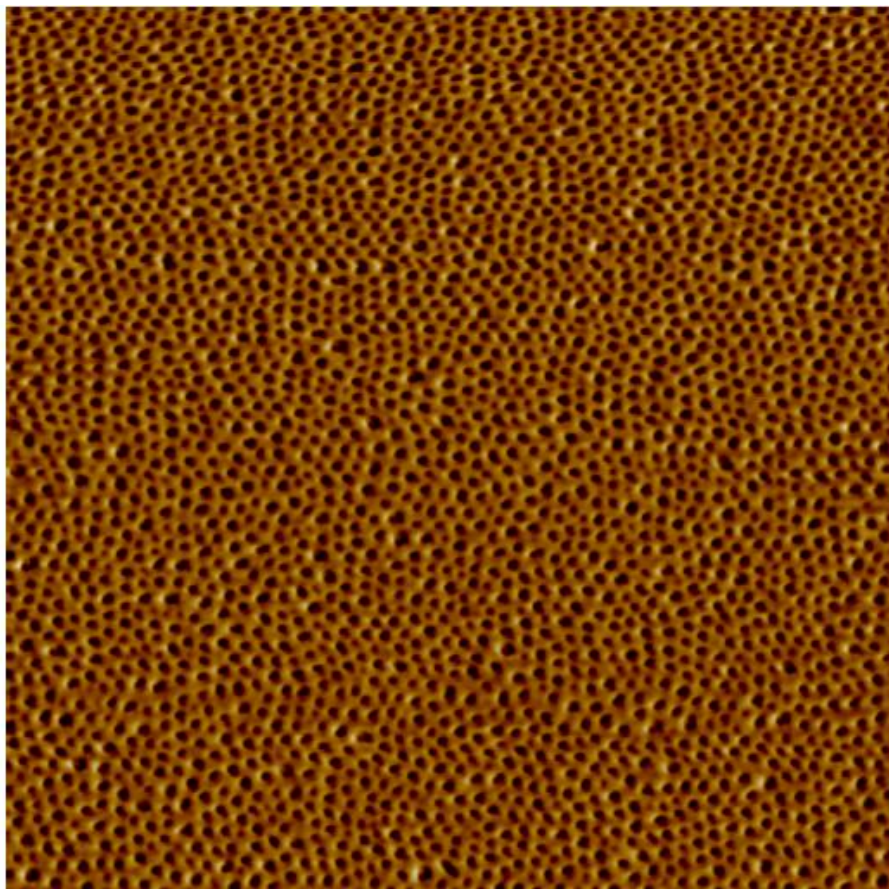
*Adv. Mater.* **18** 709 (2006)



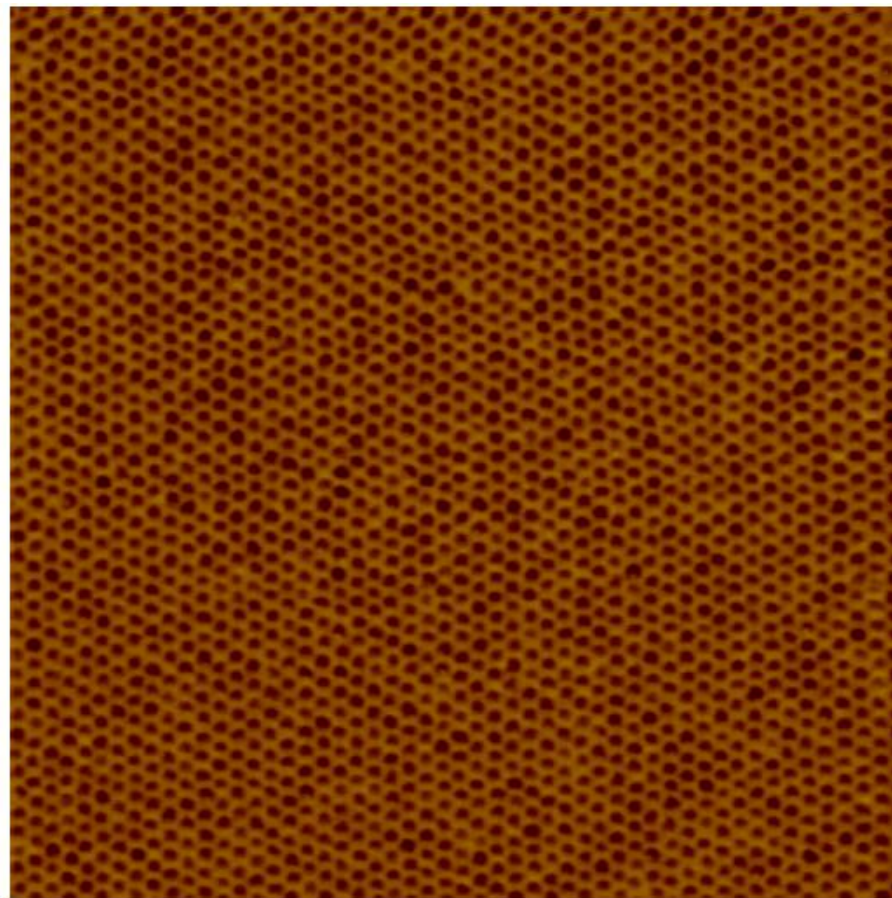


# ***PS-*b*-PEO (19.0k-6.3k)***

**As-spun film (~120 *nm*)**



**Solvent annealed film**





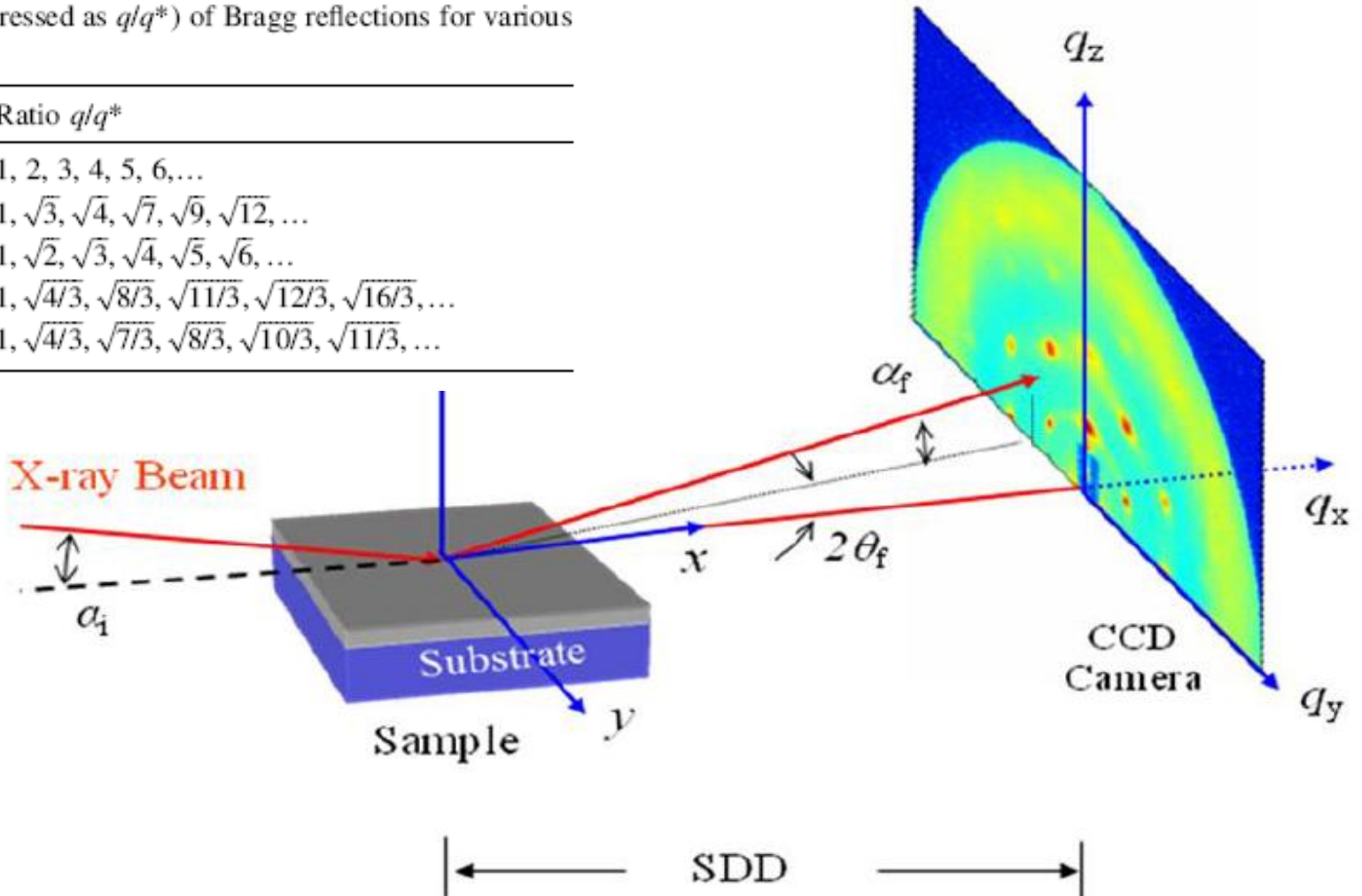
# Grazing Incidence X-ray Scattering

$$I(q) \propto (\Delta\rho)^2 \times |E(\alpha)|^2 \times |E(\beta)|^2 \times |F_s(q)|^2 \times |S_s(q)| \times |F_c(q)|^2$$

Table 1

Peak positions (expressed as  $q/q^*$ ) of Bragg reflections for various structures

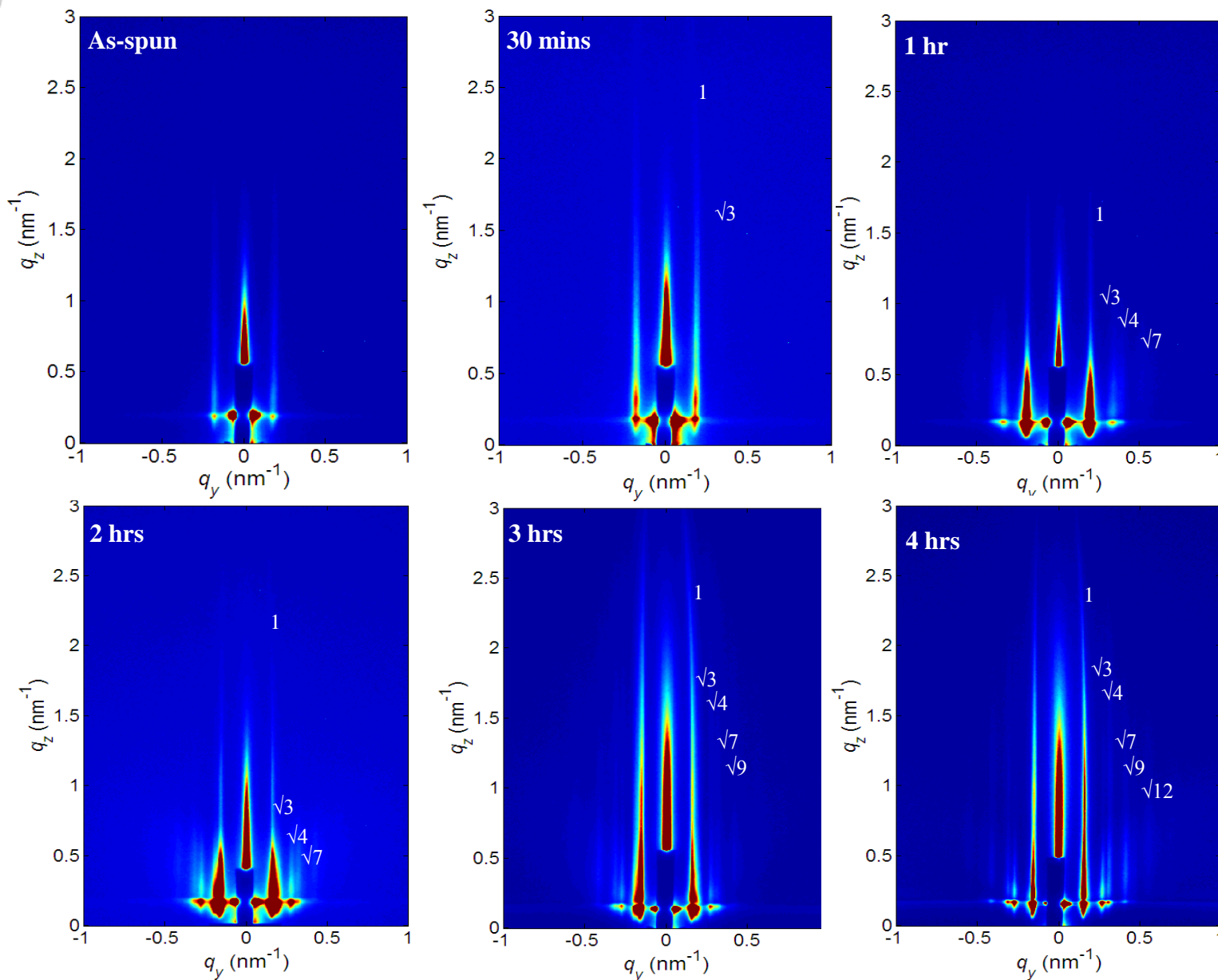
Structure	Ratio $q/q^*$
Lam	1, 2, 3, 4, 5, 6, ...
Hex ( $p6mm$ )	$1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}, \sqrt{12}, \dots$
BCC ( $Im\bar{3}m$ )	$1, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}, \sqrt{6}, \dots$
FCC ( $Fm\bar{3}m$ )	$1, \sqrt{4/3}, \sqrt{8/3}, \sqrt{11/3}, \sqrt{12/3}, \sqrt{16/3}, \dots$
Gyr ( $Ia\bar{3}d$ )	$1, \sqrt{4/3}, \sqrt{7/3}, \sqrt{8/3}, \sqrt{10/3}, \sqrt{11/3}, \dots$





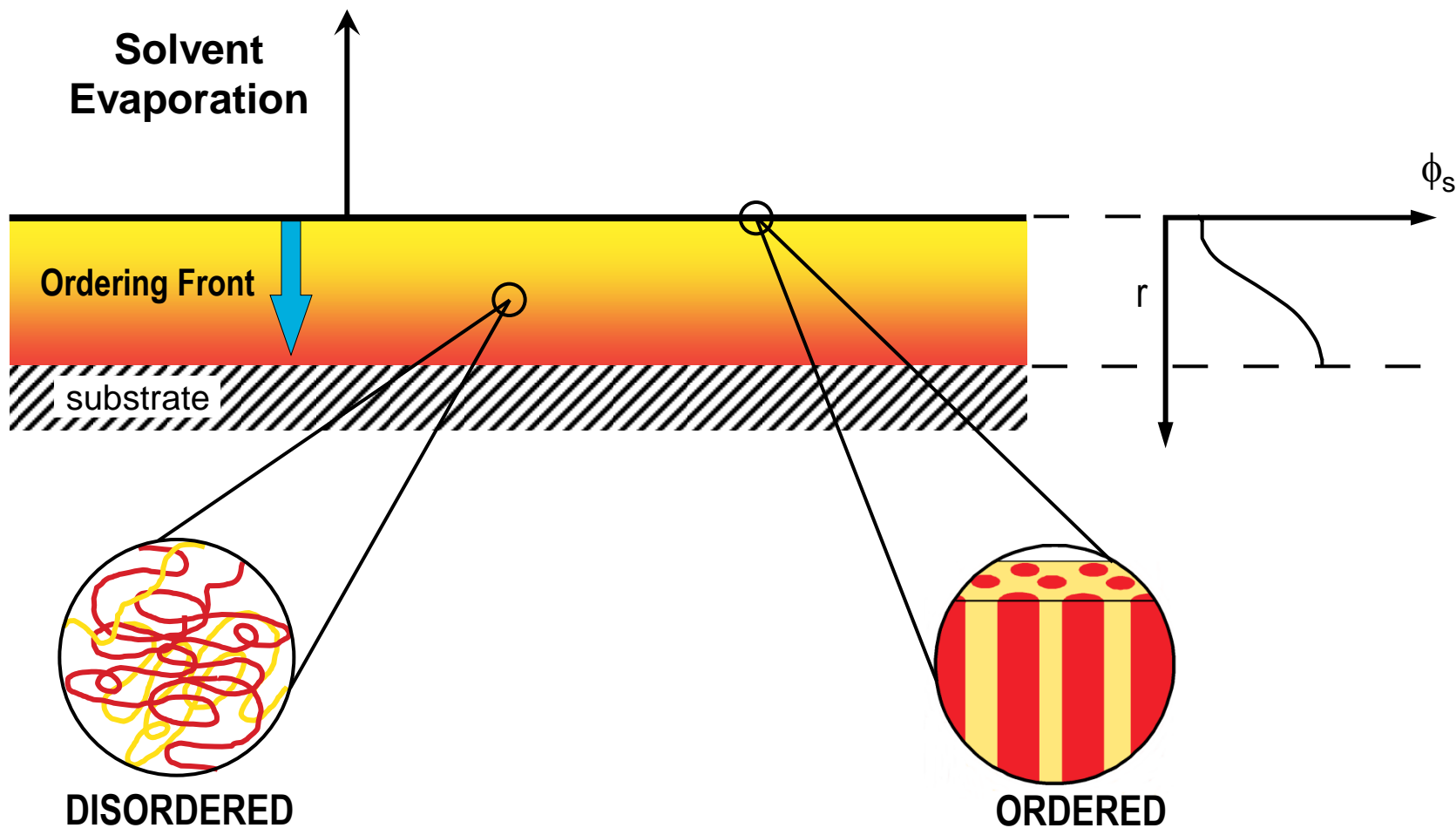


# ***GISAXS Patterns of PS-*b*-P4VP Thin Films***





# *Schematic diagram of solvent evaporation*

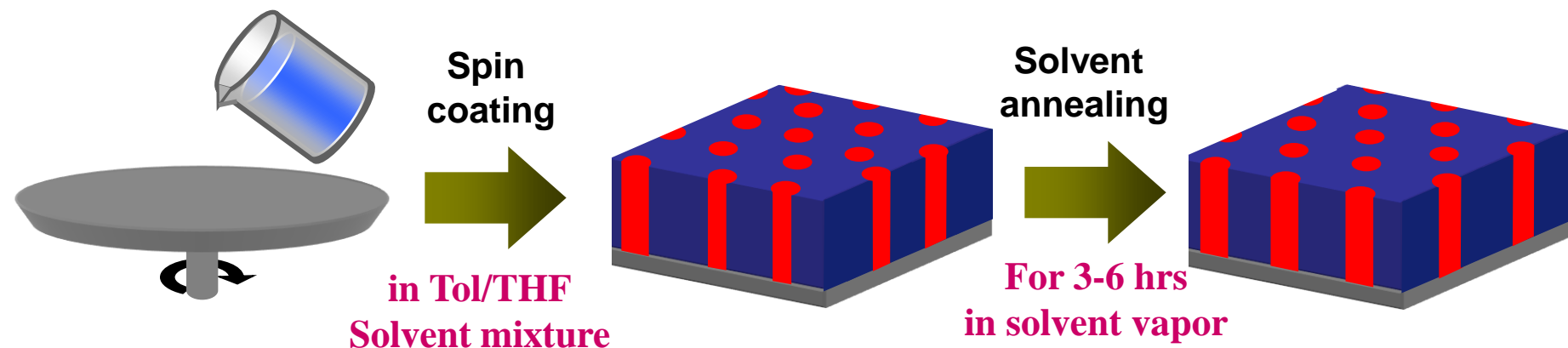




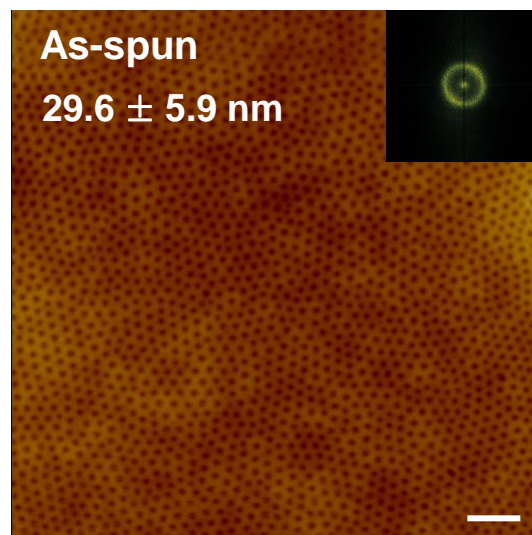


# Schematic Diagram of Template Preparation

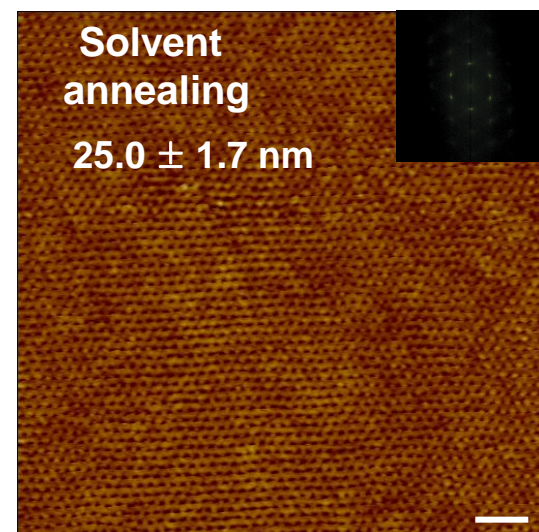
**Polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP)**



**SFM  
Images**



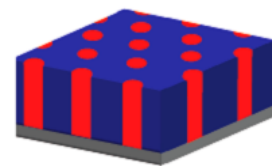
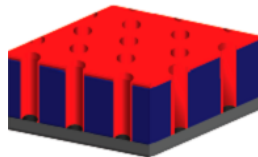
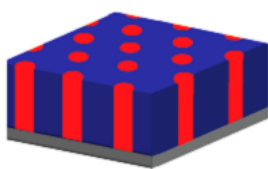
Scale bars: 200nm



S. Park et al. *ACS Nano* **2008**, 2, 766

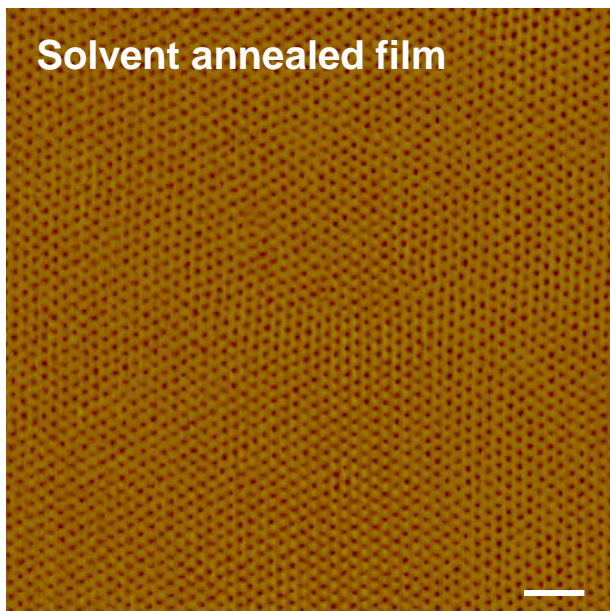


# *Reversible Reconstruction*

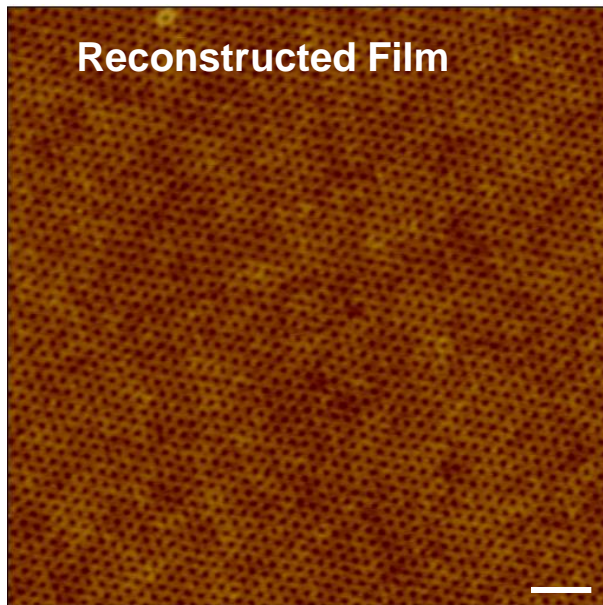


**SFM image**

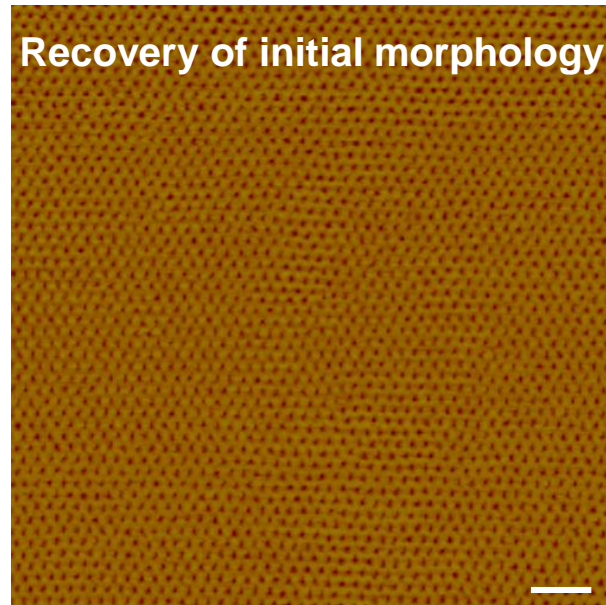
**Solvent annealed film**



**Reconstructed Film**



**Recovery of initial morphology**



**Solvent annealing  
in Toluene/THF**

**Immersion in EtOH  
for 20 min**

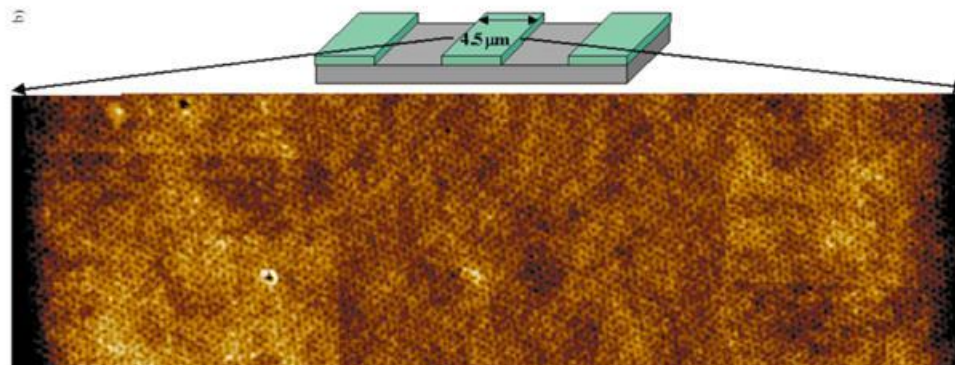
**Thermal annealing  
at 115 °C for 10 min**

**Scale Bars: 200 nm**

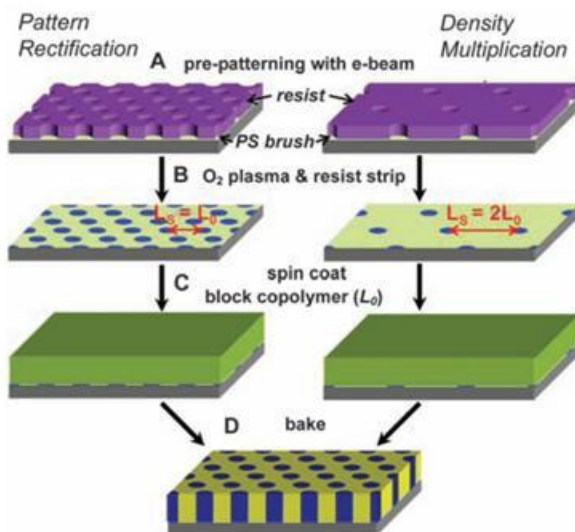
**(PS-b-P4VP: 47.6k-20.9k)**



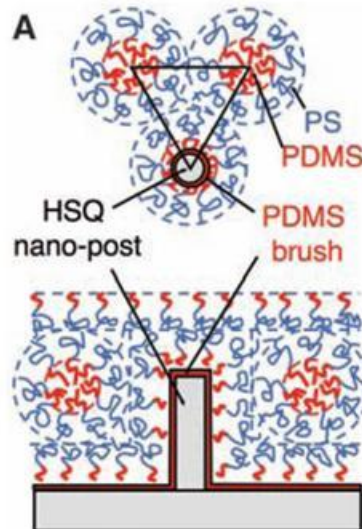
To overcome grain size limitation: Lithography Techniques



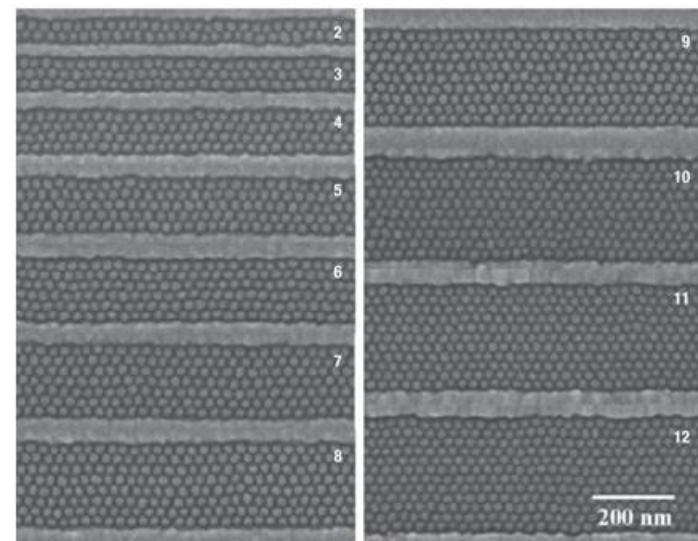
Kramer and Coworkers  
*Adv. Mater.* **2001**, 13, 1152



Nealey and Coworkers  
*Science* **2008**, 321, 936



Berggren and Coworkers  
*Science* **2008**, 321, 939



Ross and Coworkers  
*Nat. Mater.* **2004**, 3, 823

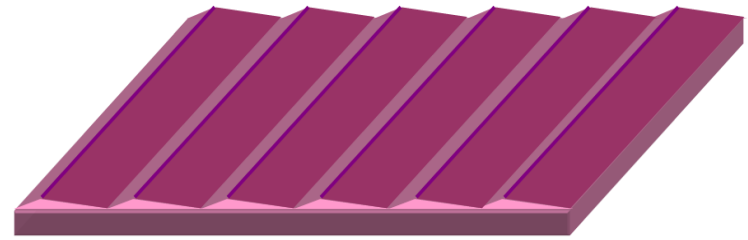


# *Macroscopic Arrays of BCP Microdomains*

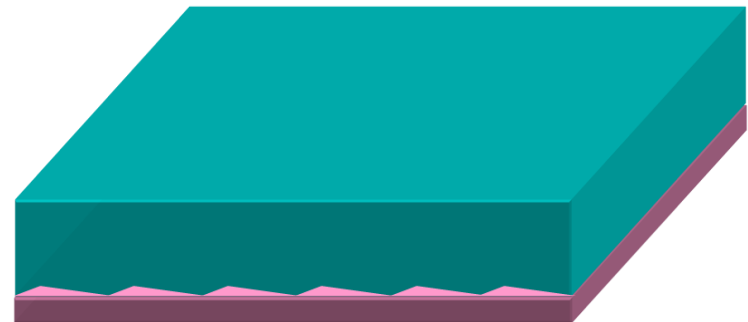


**Mis-cut Single Crystal**

→  
**Thermal  
Annealing**

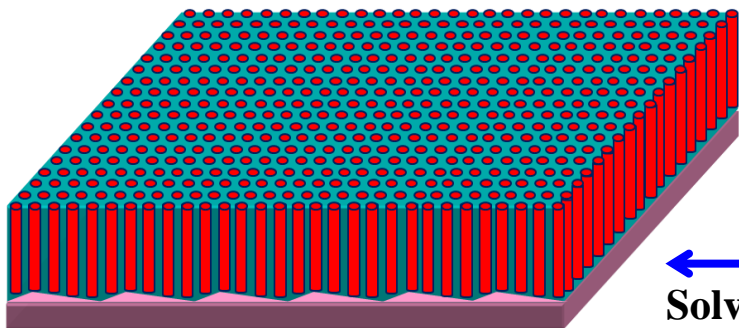


**Sawtooth Pattern**



**Spin-Coated BCP Film**

←  
**Solvent  
Annealing**



**Highly Ordered  
BCP Films**

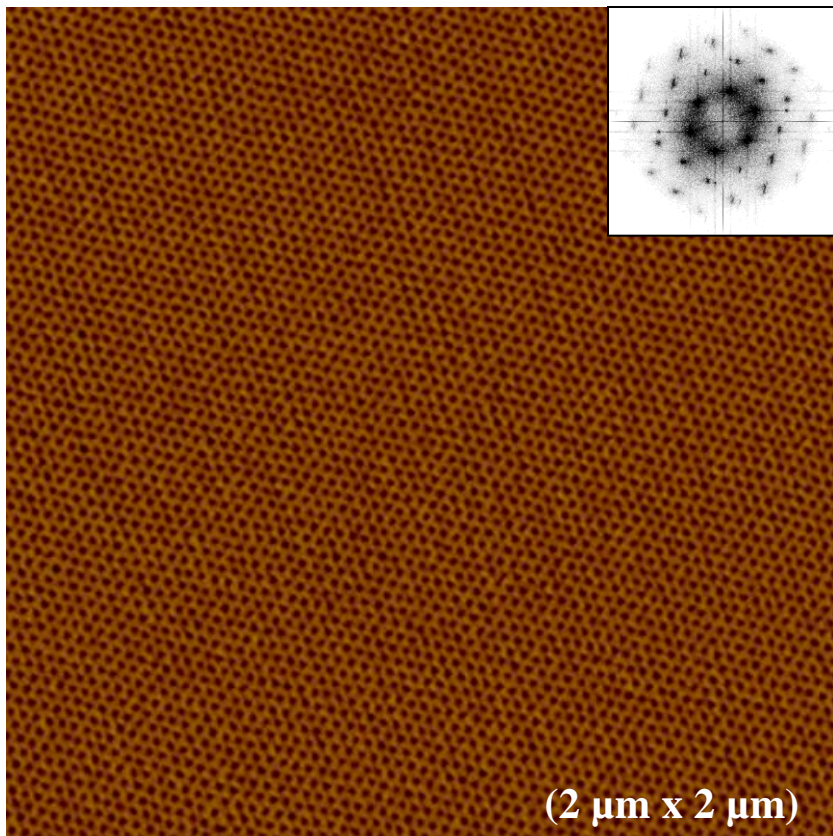




# *Highly Ordered PS-*b*-PEO Microdomains*

**PS-*b*-PEO (20k-6.5k)**

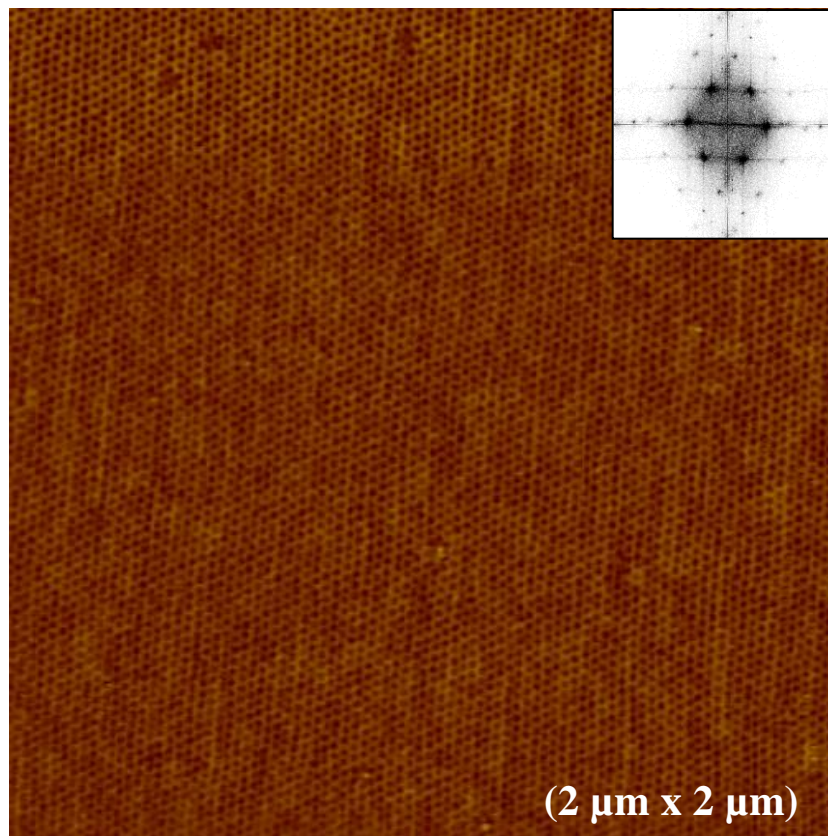
**Phase mode**



**d-spacing: 30.2 nm**  
**Feature size: ~13 nm**  
**0.74 Terabit/inch<sup>2</sup>**

**PS-*b*-PEO (19k-6.4k)**

**Phase mode**



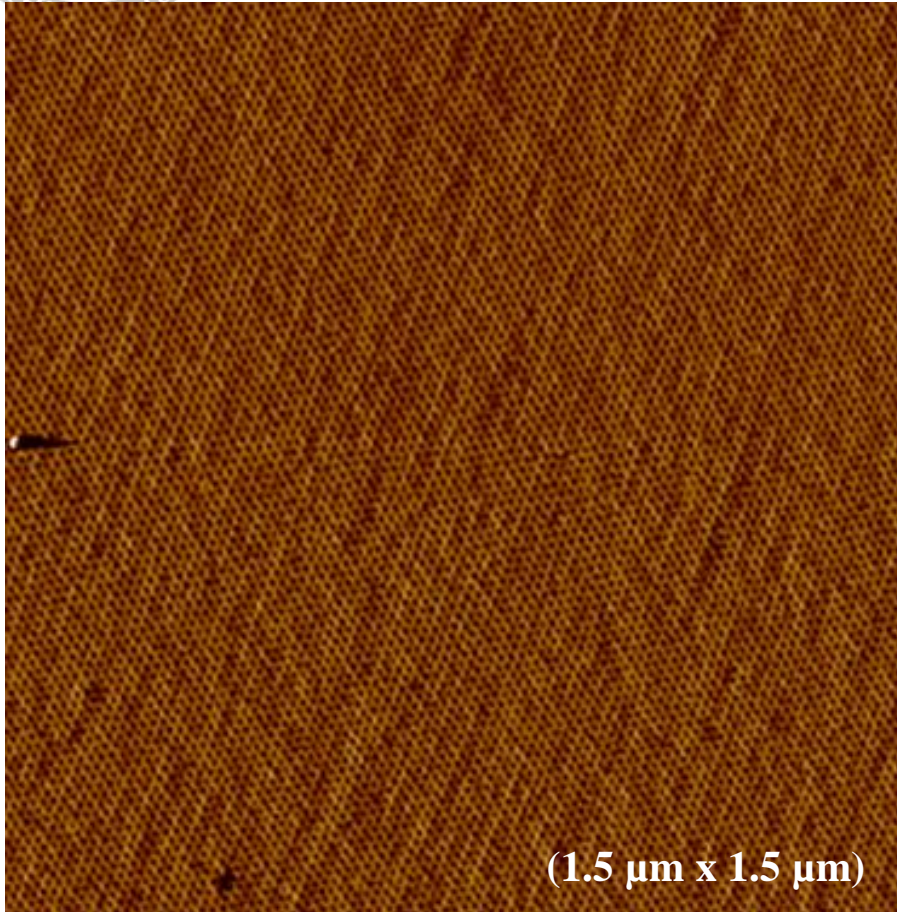
**d-spacing: 24.4 nm**  
**Feature size: 9.5 nm**  
**1.21 Terabit/inch<sup>2</sup>**





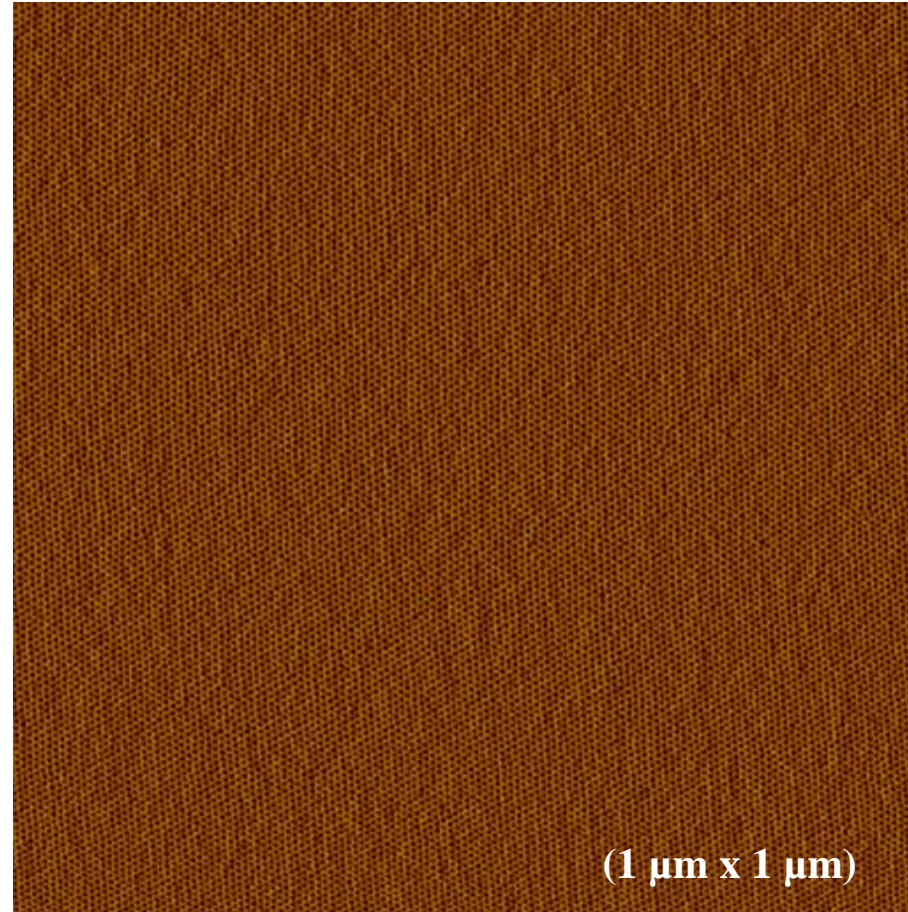
# *Highly Ordered PS-*b*-PEO Microdomains*

**PS-*b*-PEO (16k-5k)**



**d-spacing: ~18.1 nm**  
**Feature size: ~ 7.8 nm**  
**2.42 Terabit/inch<sup>2</sup>**

**PS-*b*-PEO (5k-2k) (Au complex)**



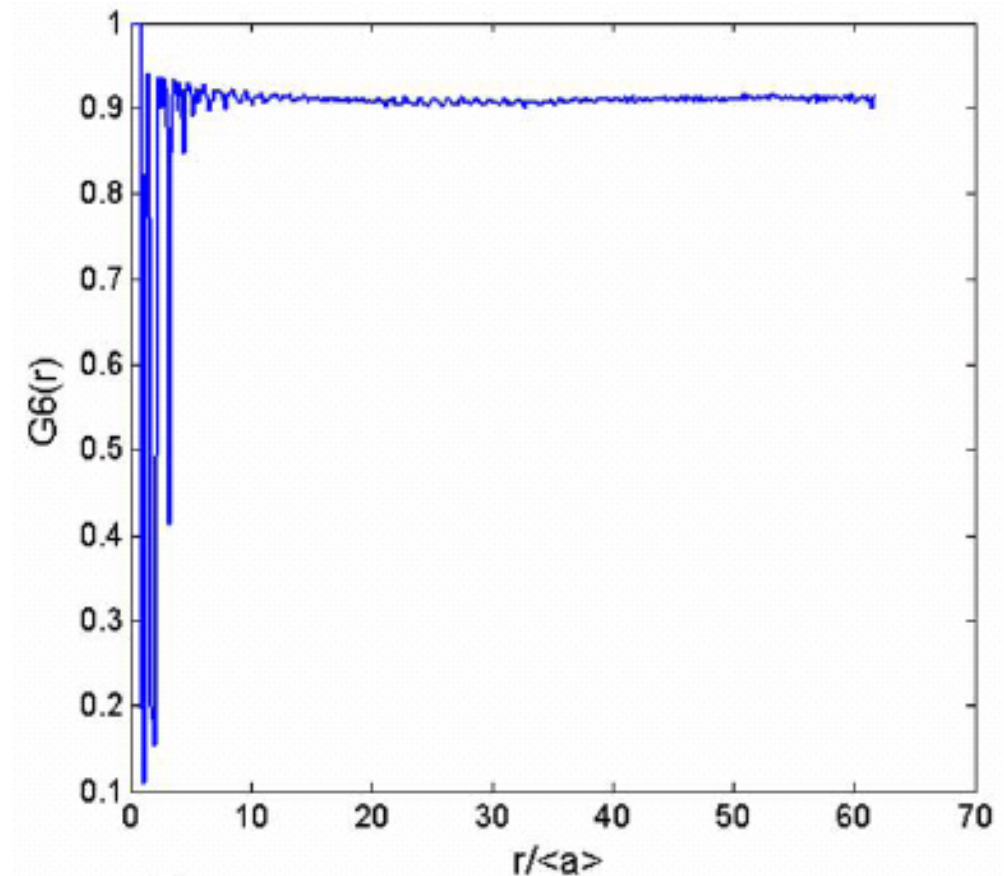
**d-spacing: 6.93 nm**  
**Feature size: ~ 3.1 nm**  
**10.5 terabit/inch<sup>2</sup>**



# *Orientational Ordering*

$$G_6(r) = \langle \varphi_6^*(0) \varphi_6(r) \rangle$$

$$\varphi_6(r_j) = \frac{\sum_{j=1}^{NN} \exp(6i\theta(r_{ij}))}{NN}$$



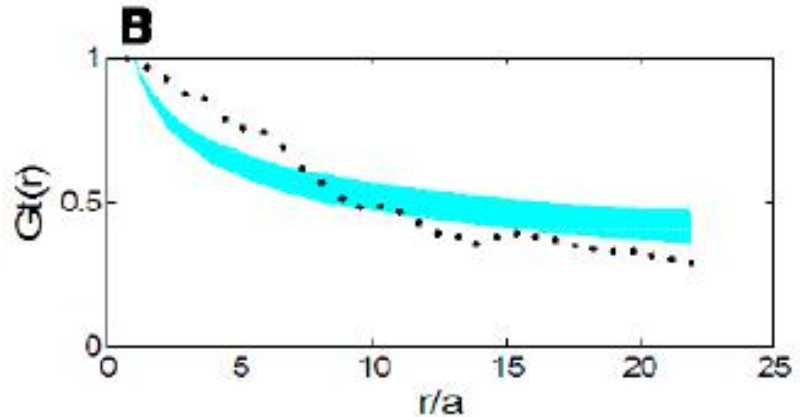
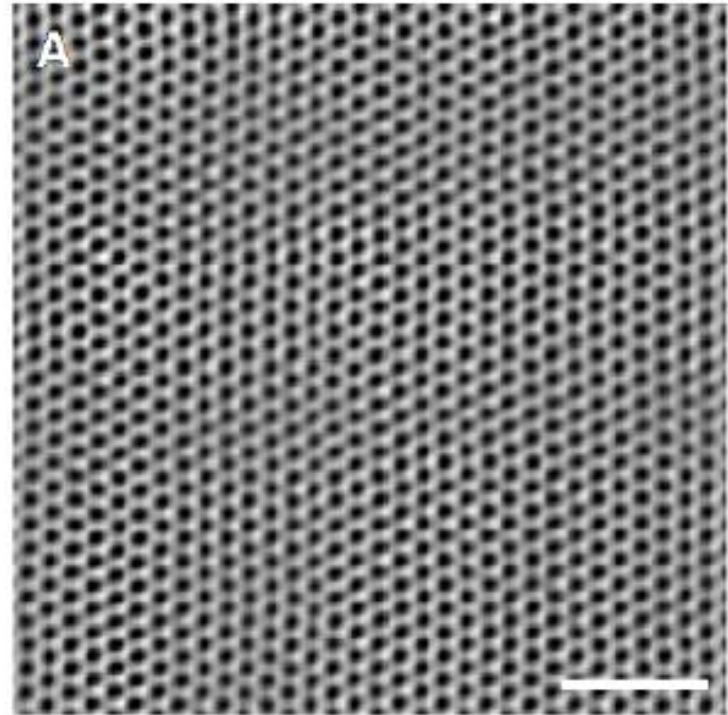




# *Translational Ordering*

$$G_T(r) = \langle e^{i\vec{K} \cdot \vec{r}^1} e^{i\vec{K} \cdot (\vec{r}^1 - \vec{r})} \rangle$$

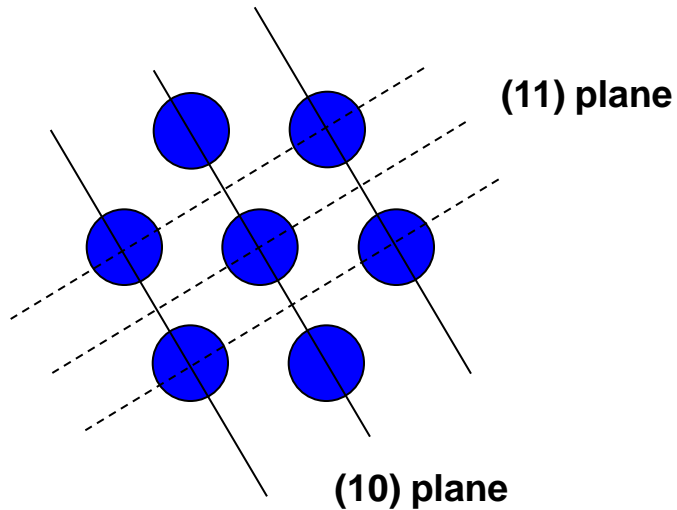
$$G_T(r) \propto \left(\frac{r}{a}\right)^{-\eta_T}$$







# *Two-Dimensional Hexagonal Lattice*



**Solid and dotted lines represent the symmetry planes perpendicular to the planes of paper**

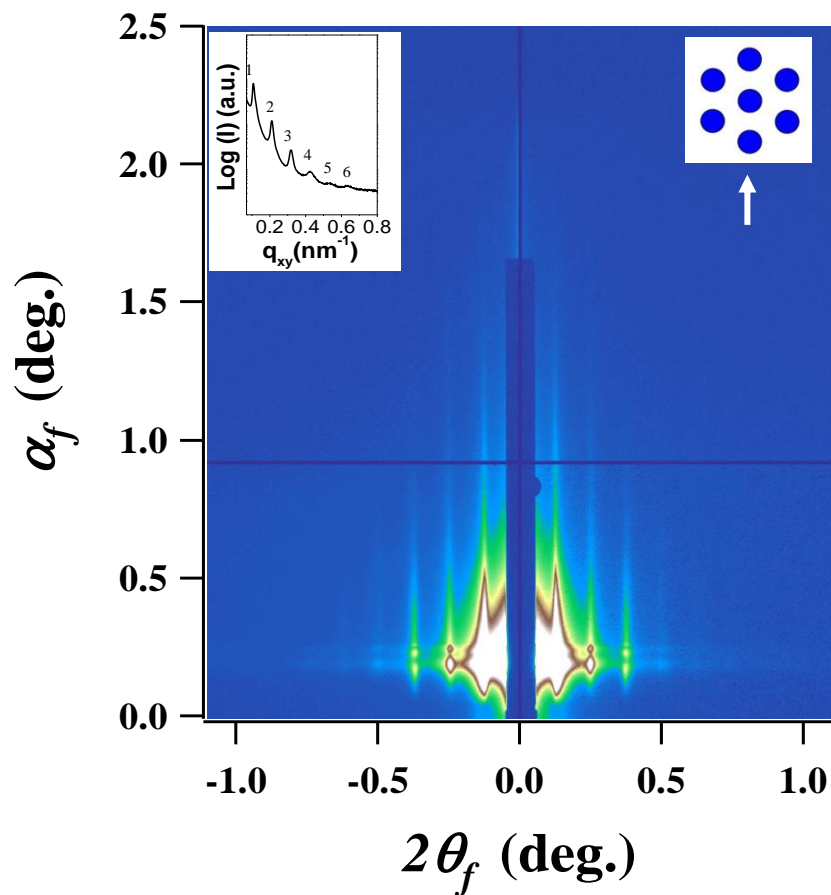
**Hexagonal lattice: (10), (11), (20), (21), (30), (22), (31), etc.**

**Diffraction peaks: 1,  $\sqrt{3}$ ,  $\sqrt{4}$ ,  $\sqrt{7}$ ,  $\sqrt{9}$ ,  $\sqrt{12}$ , etc.**

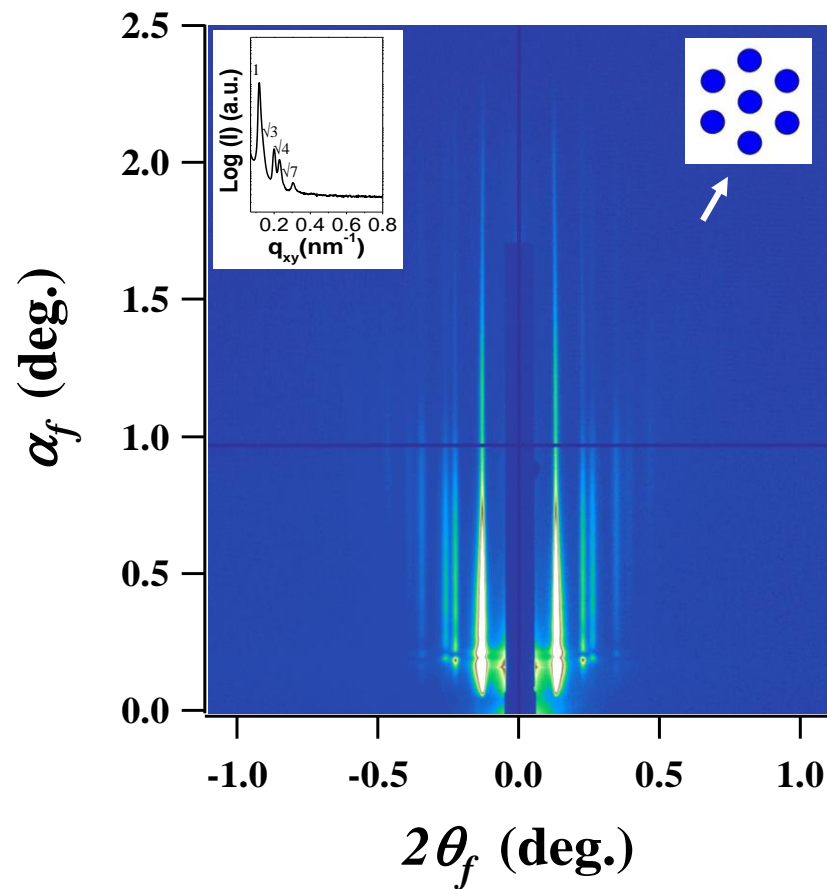


# *GISAXS Patterns of Highly Ordered BCPs*

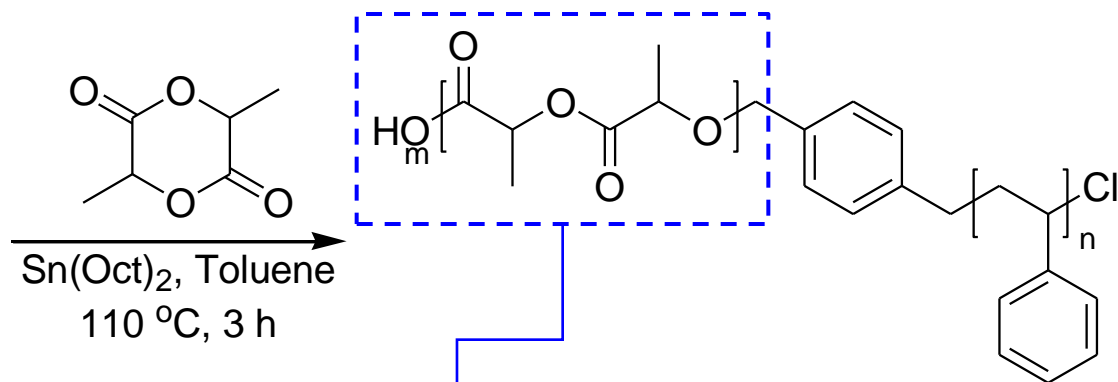
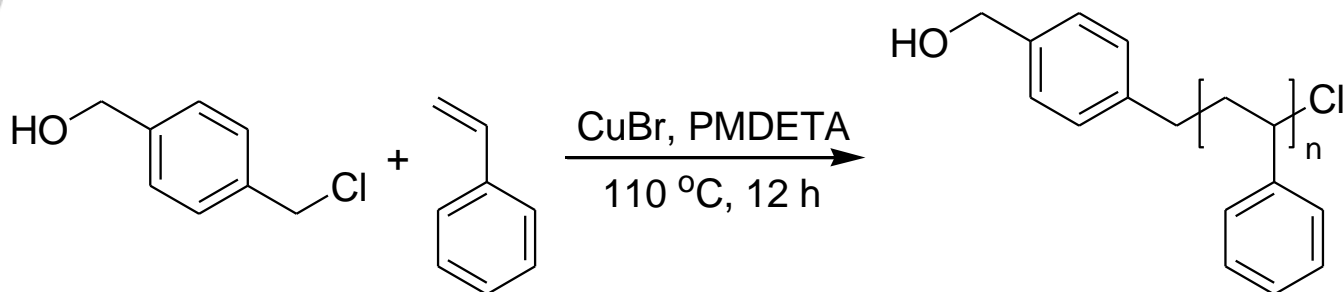
Sample stage:  $0^\circ$



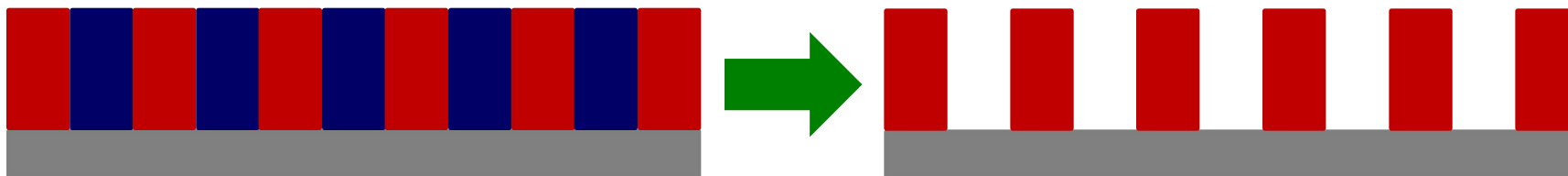
Sample stage:  $30^\circ$

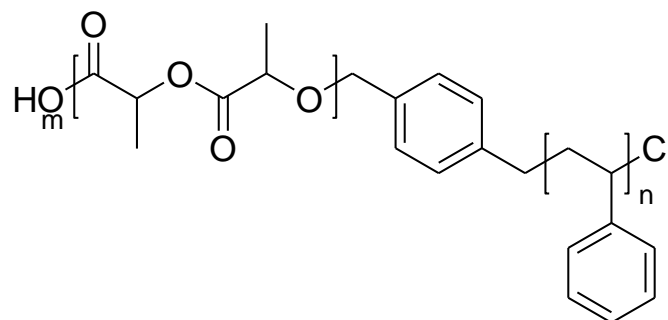






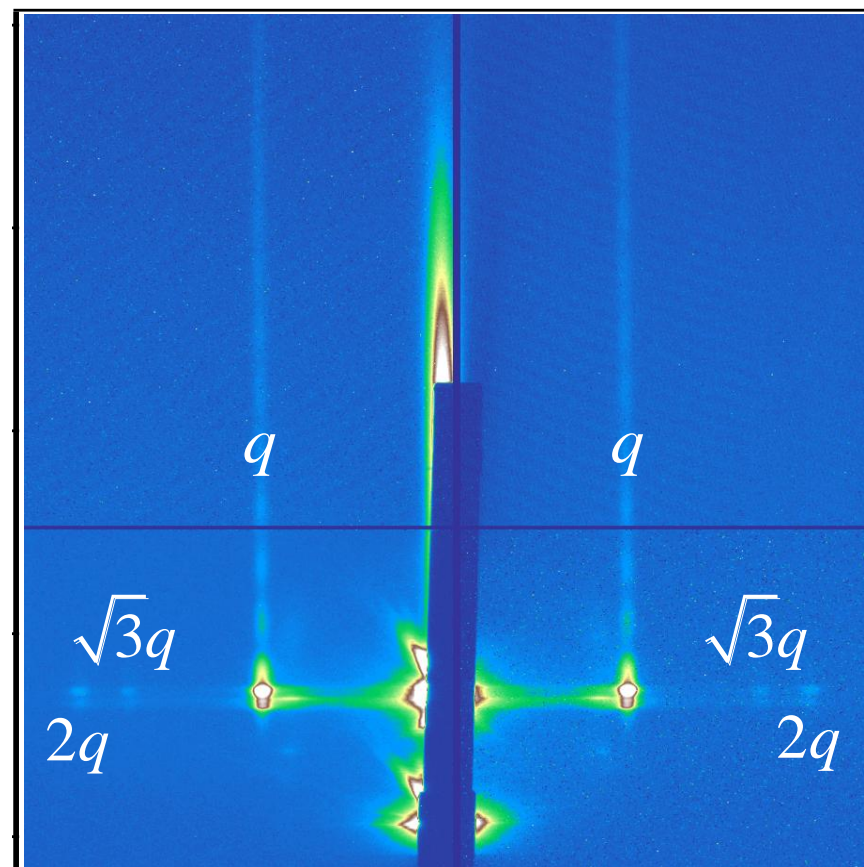
Biologically and Chemically Degradable Polymer



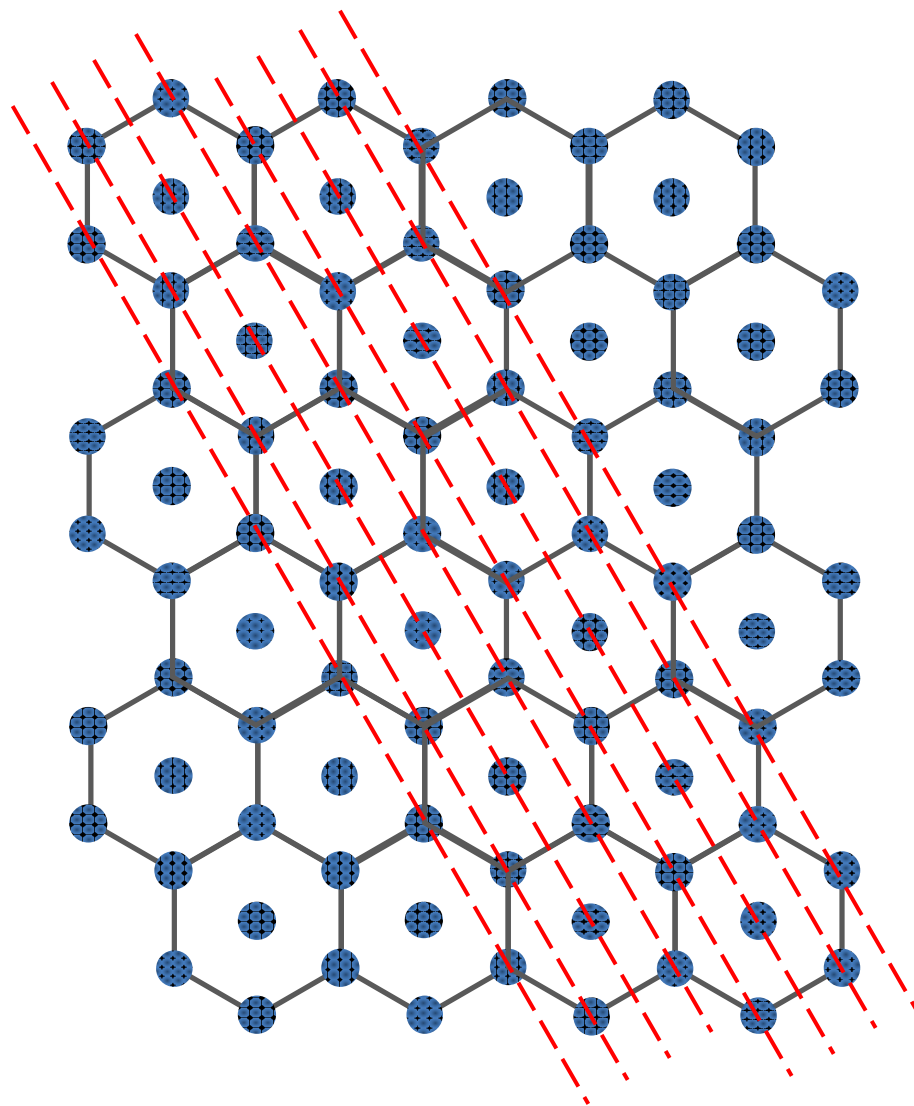
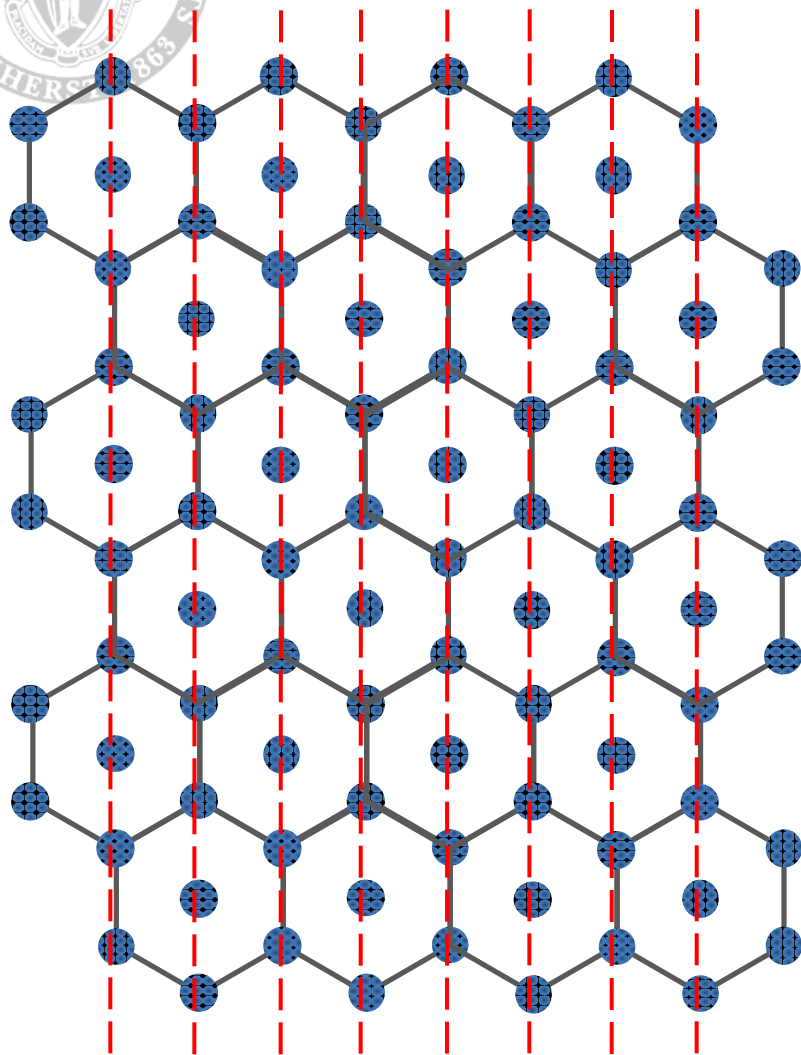


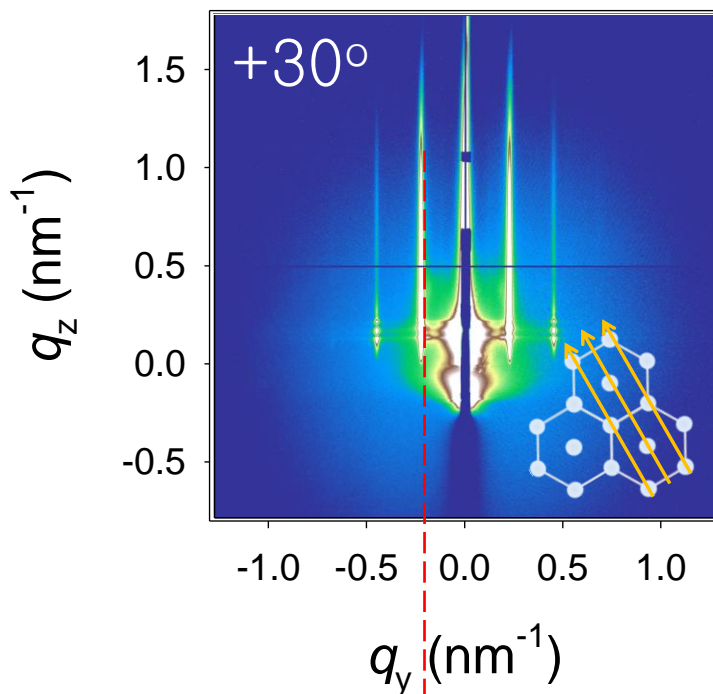
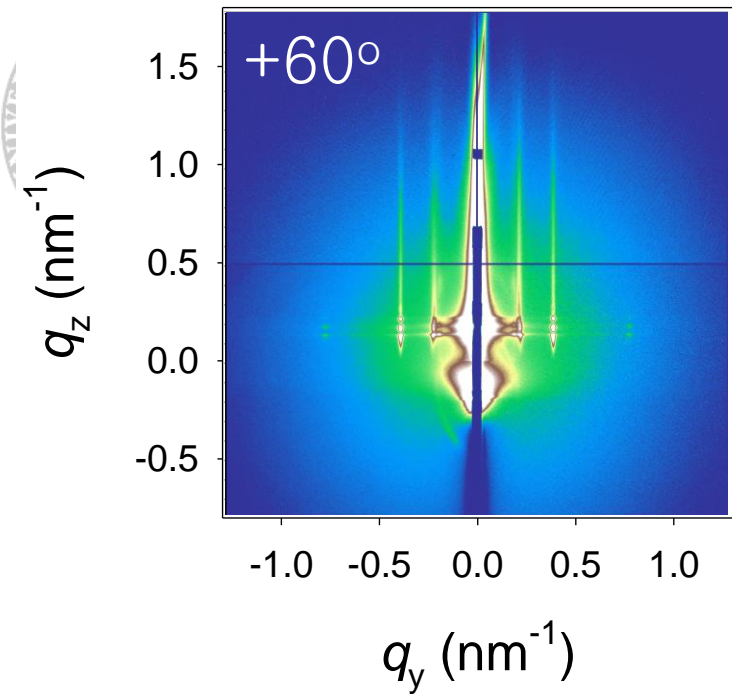
Hexagonal Packing  
on Flat Substrate

500 nm



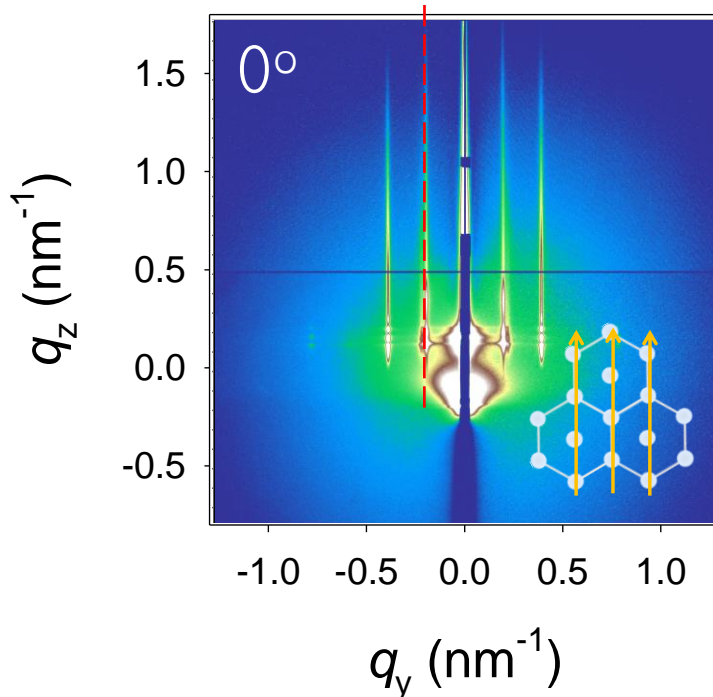
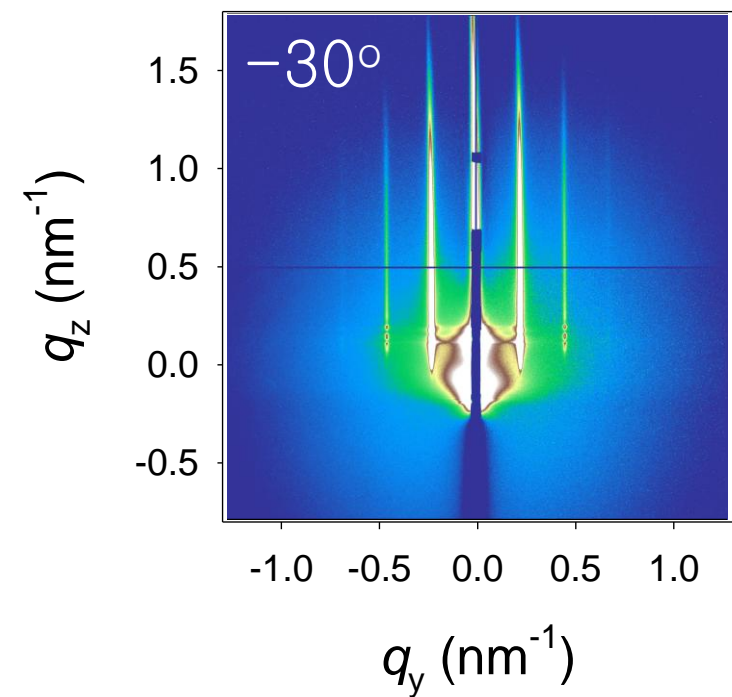






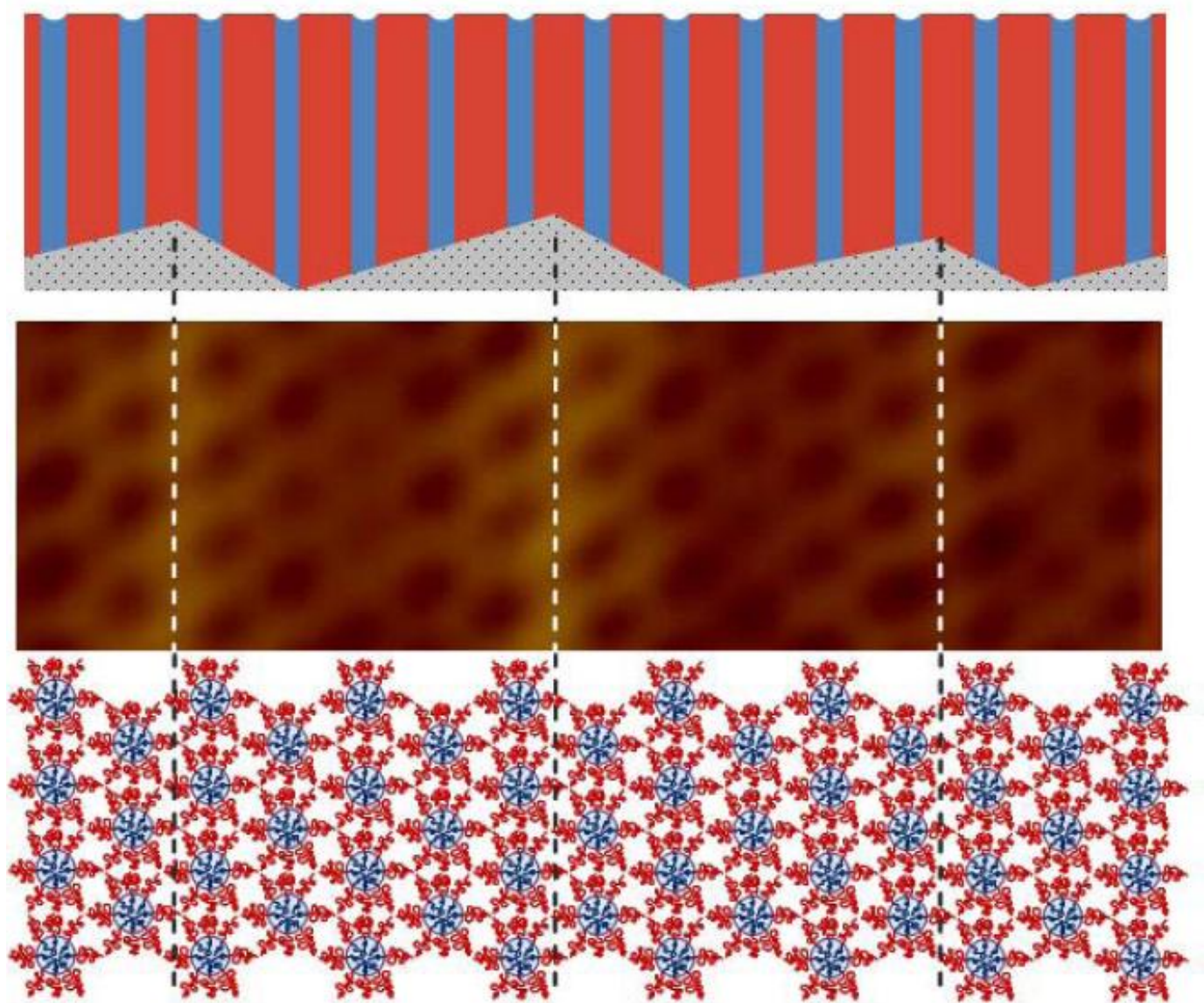
Hx Packing  
of PS-*b*-PLA  
on  
Faceted Substrate

$$d_{+00} > d_{+300}$$





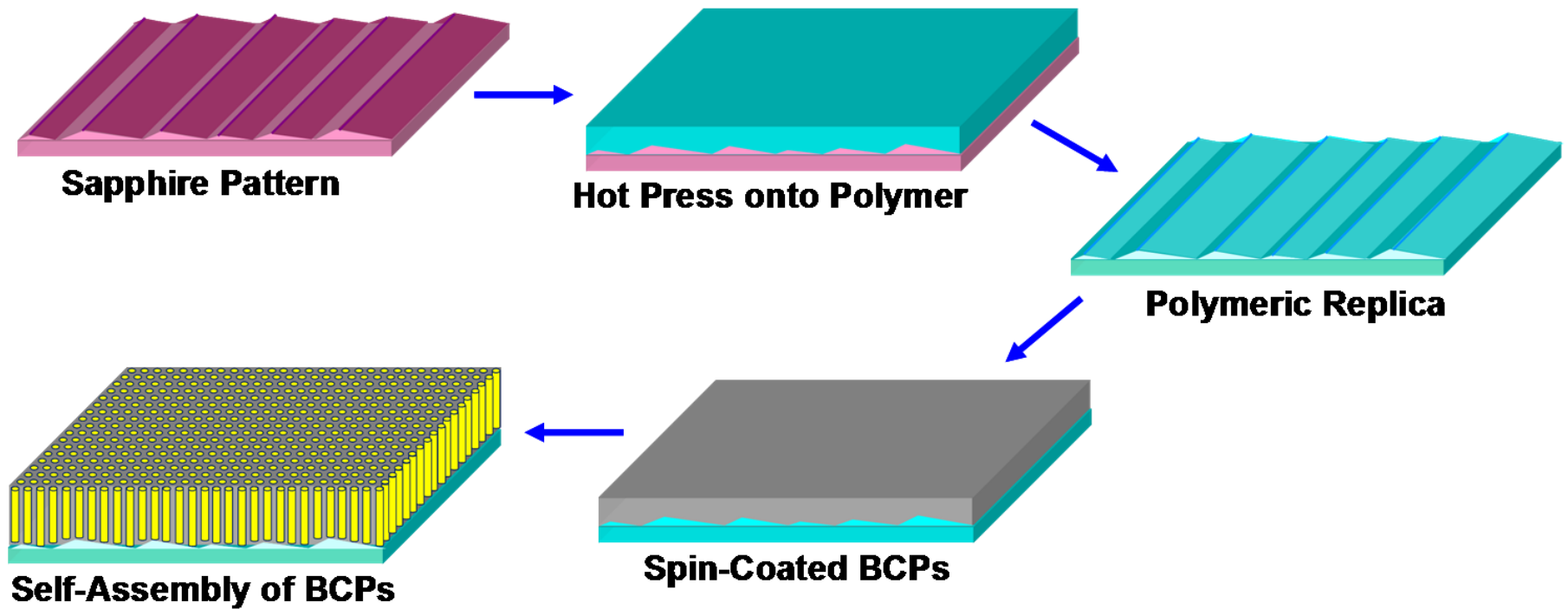
# *BCP Ordering Relative to Substrate*





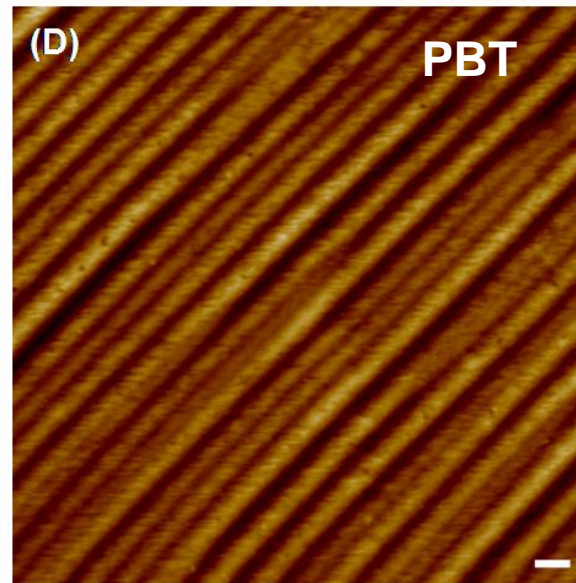
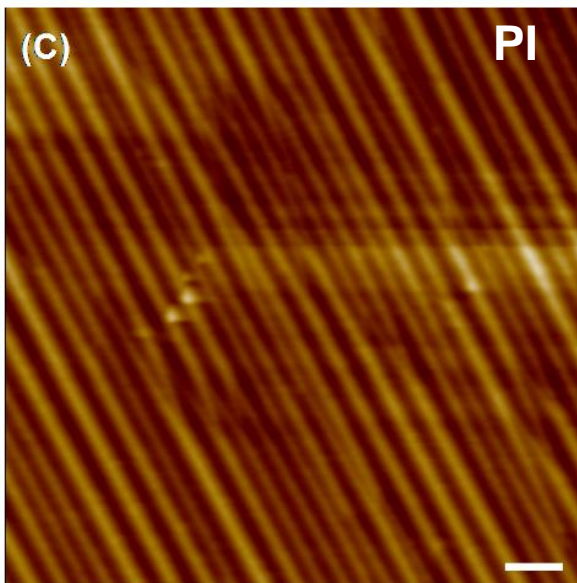
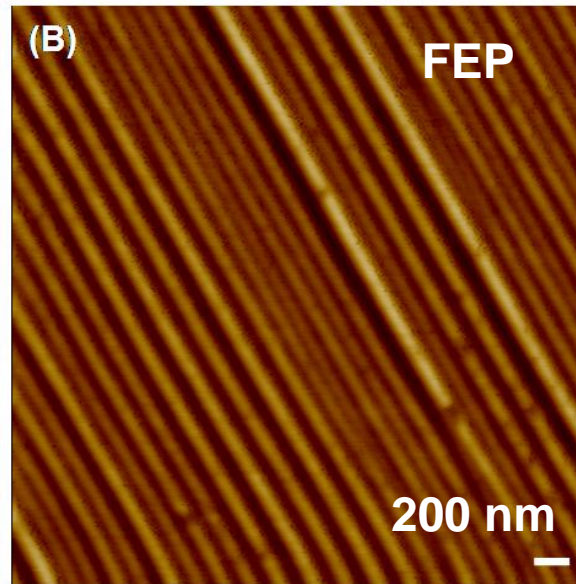
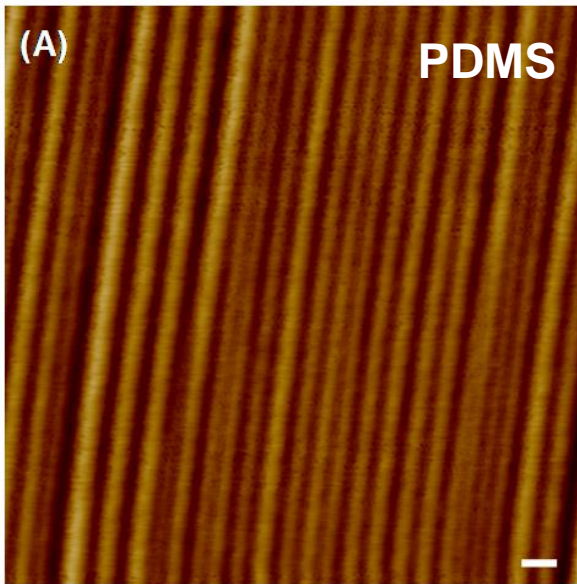


# *Pattern Transfer Process*





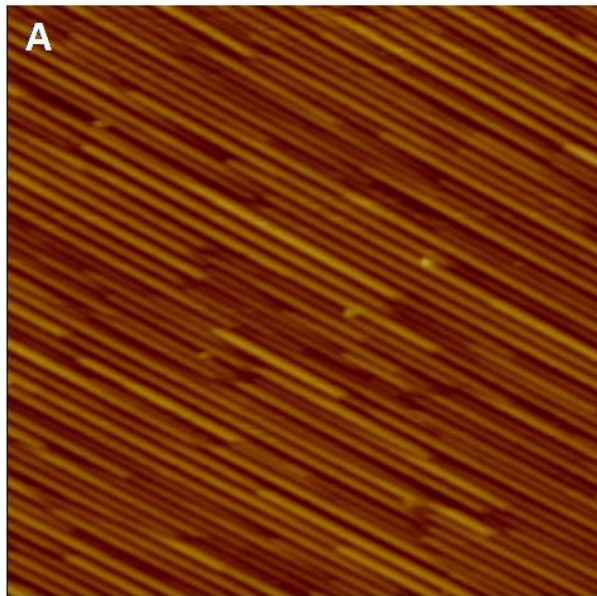
# *Topography Transfer*



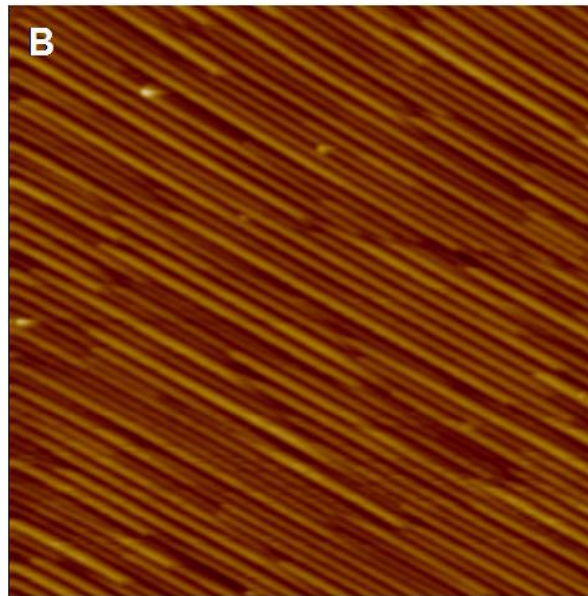


# *BCP Ordering on Soft, Flexible Substrate*

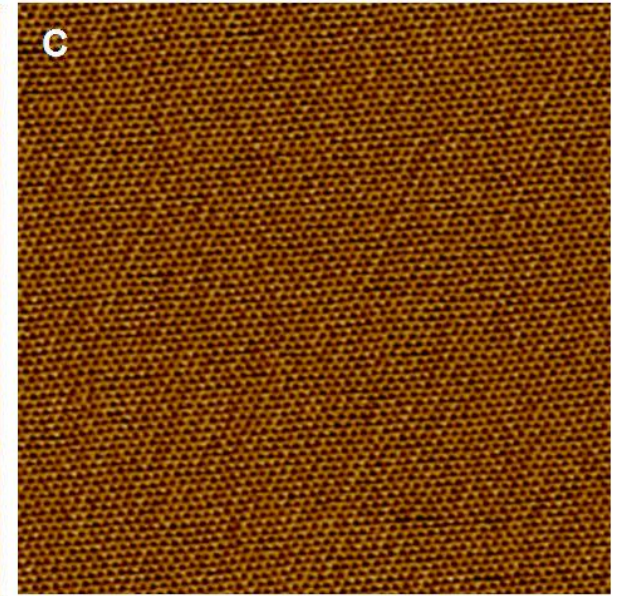
**Reconstructed Sapphire**



**PBT Replica**



**PS-*b*-PEO  
Annealed in o-xylene vapor**



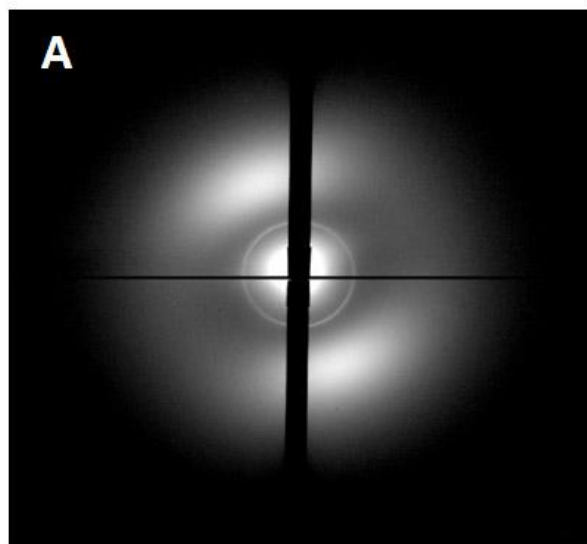
**2  $\mu\text{m}$  x 2  $\mu\text{m}$**



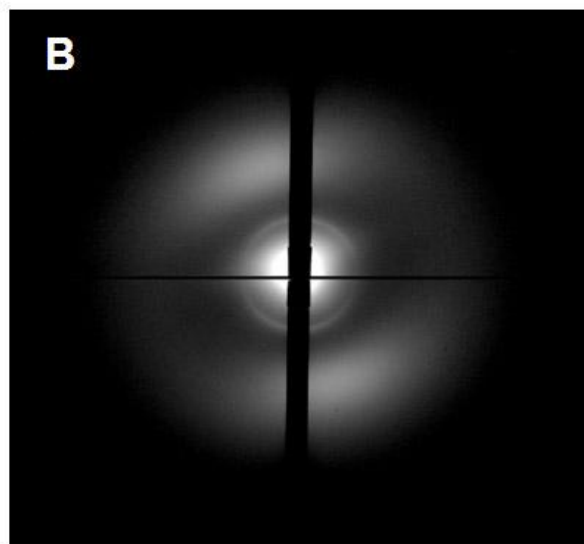


# *Transmission SAXS*

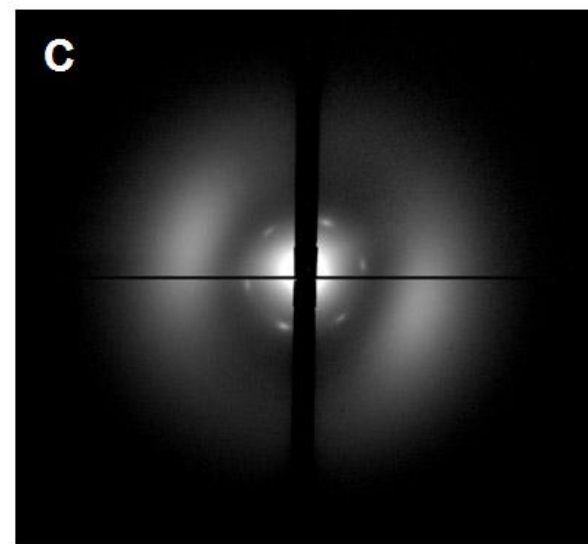
## PS-b-PEO on PBT Replica



1 hr



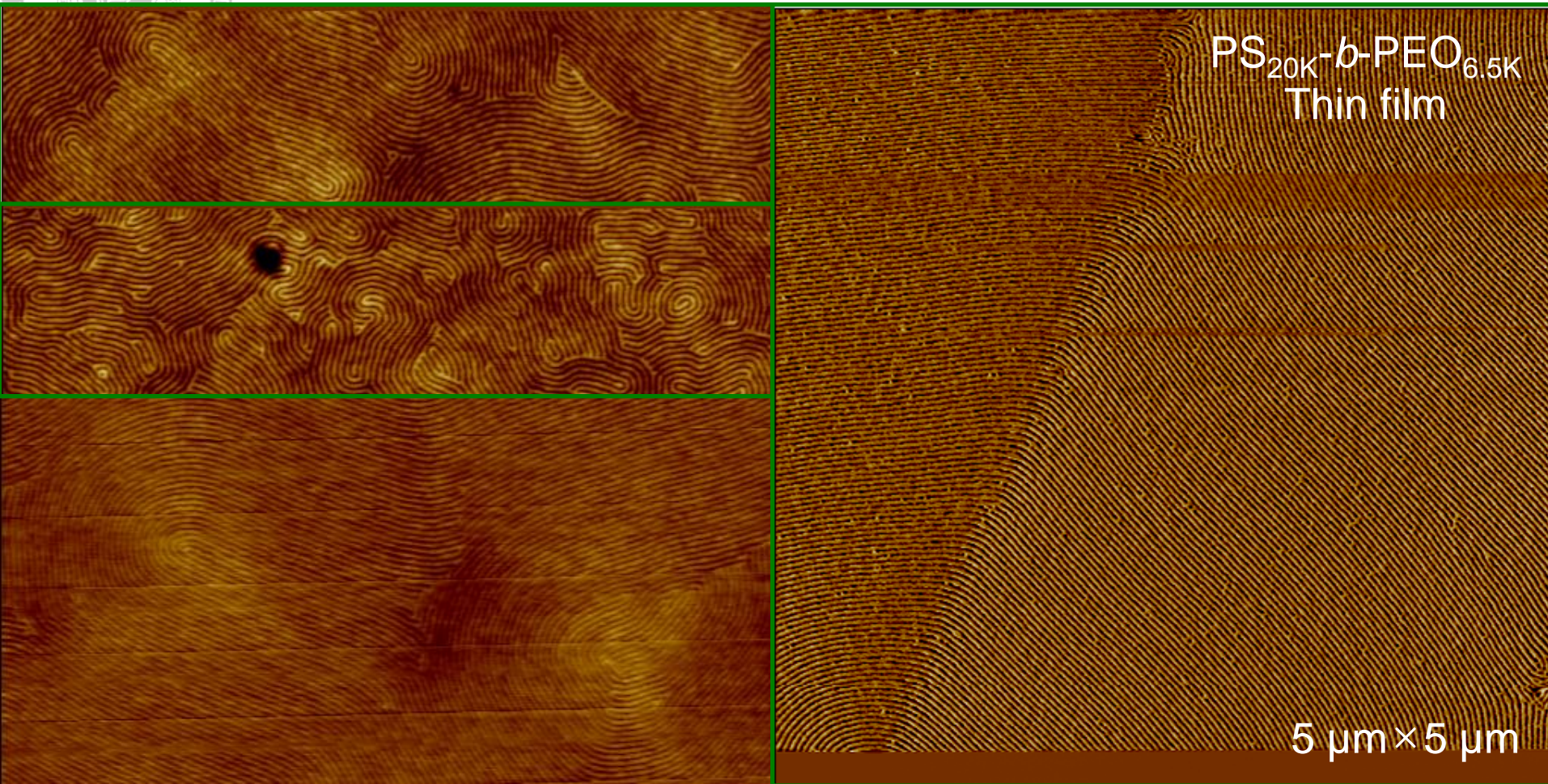
2 hr



3 hr



# *Imperfections: Parallel Alignment*



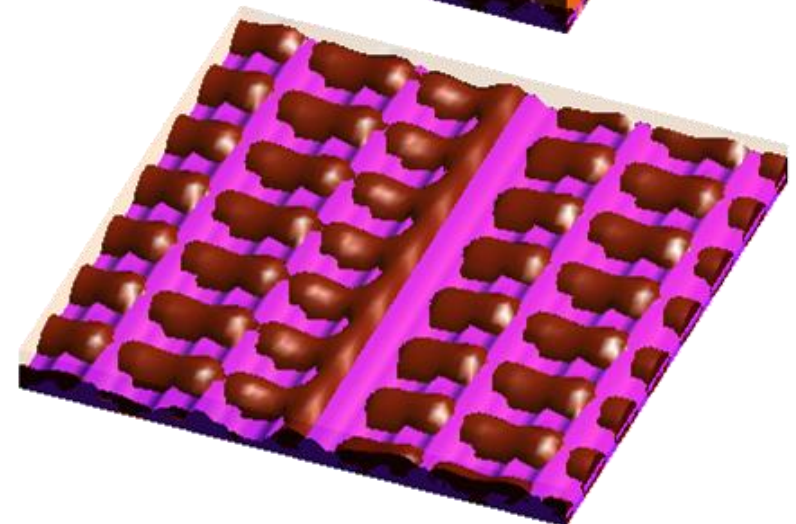
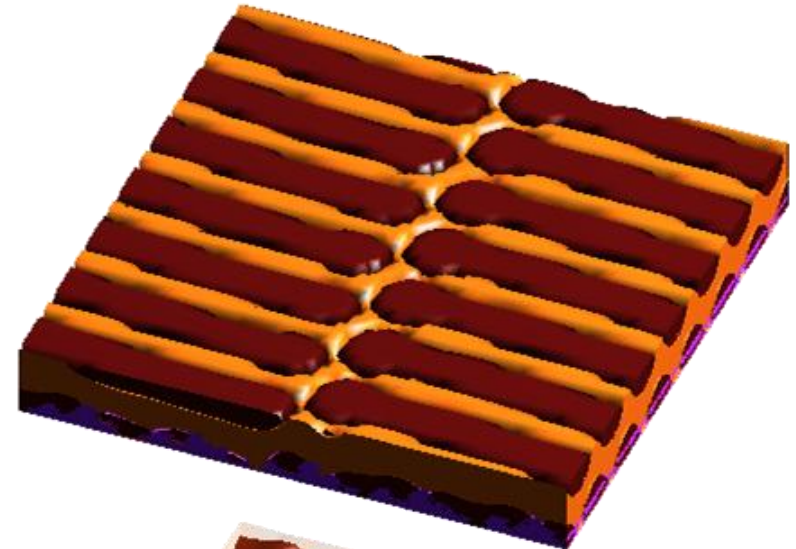
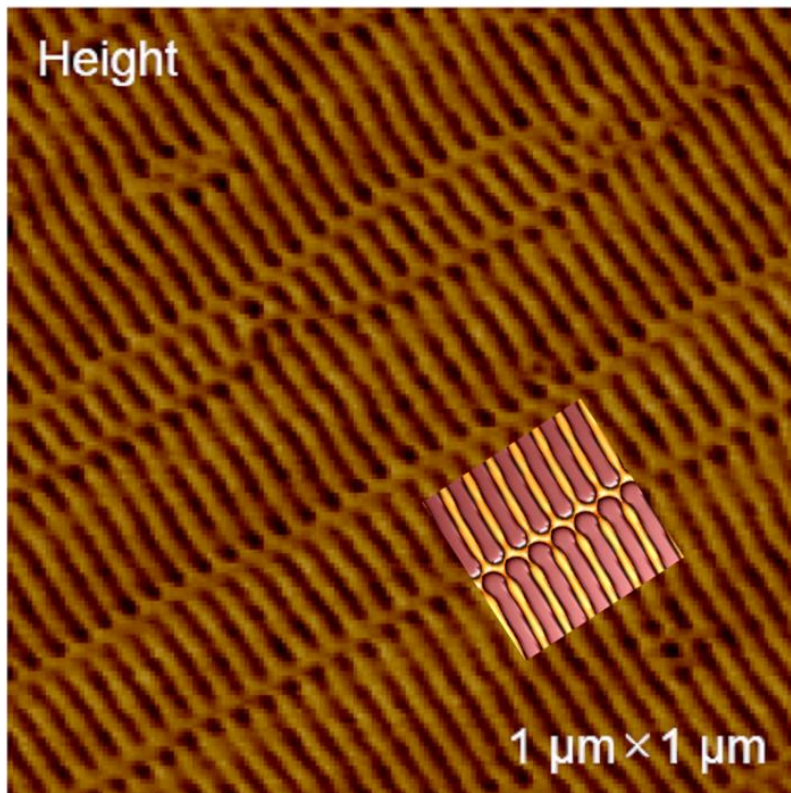
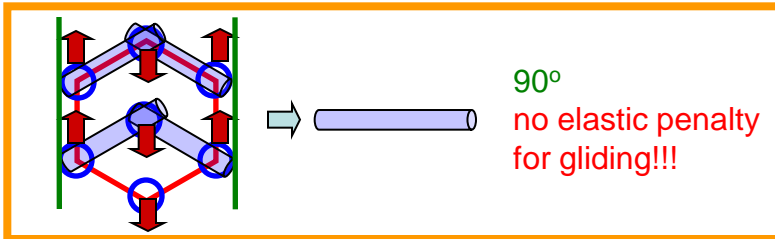




# *Parallel Alignment Perpendicular to Sawtooth*

Preliminary Results from Simulation

*J.Hu Yonsei, W.H.Jo, SNU*



(after removing major block)





# *Annihilation of Defects*

Thickness = 37 nm

Height

$1\ \mu\text{m} \times 1\ \mu\text{m}$

Thickness = 42 nm

Height

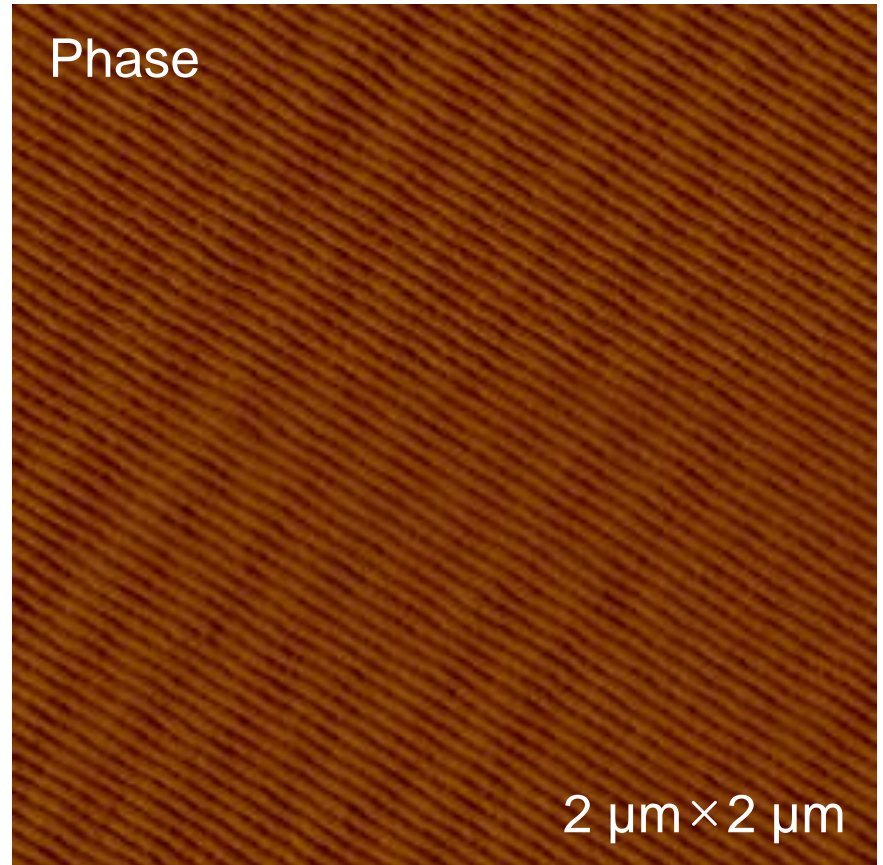
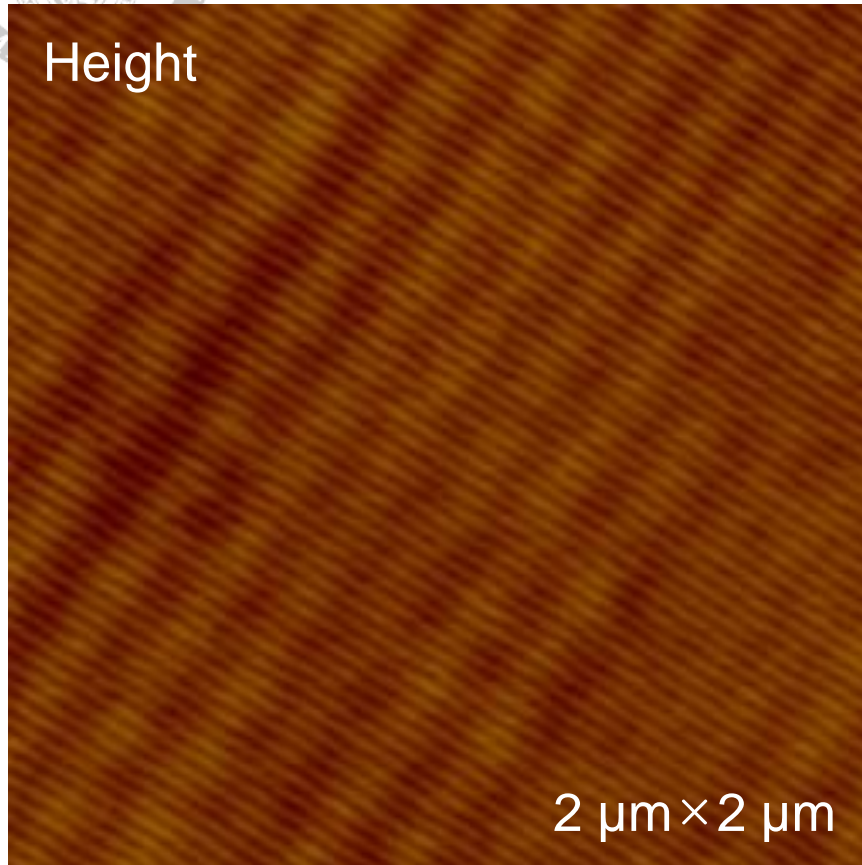
Trace of  
Annihilation

$1\ \mu\text{m} \times 1\ \mu\text{m}$

*The defects are effectively annihilated  
upon increasing the thickness!*

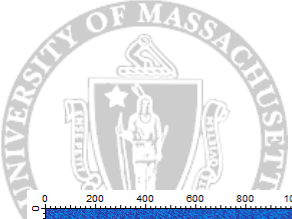


## *Line Pattern with High Degree of Straightness*

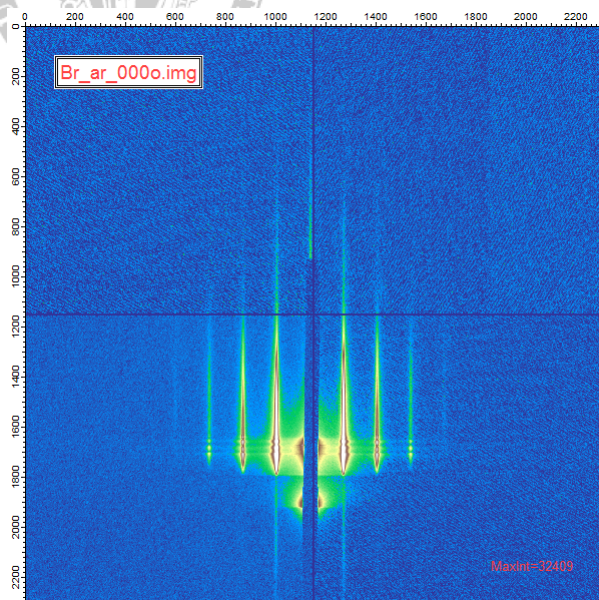


*The defects are completely annihilated  
at the optimum thickness and annealing condition!*



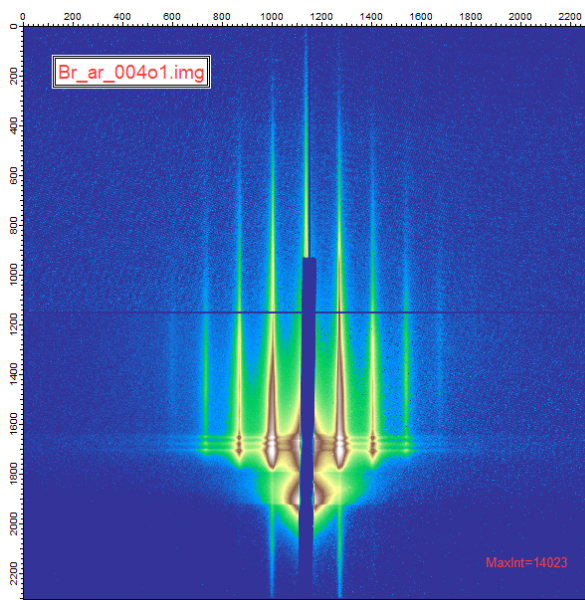


# *PERFECT or NOT?*



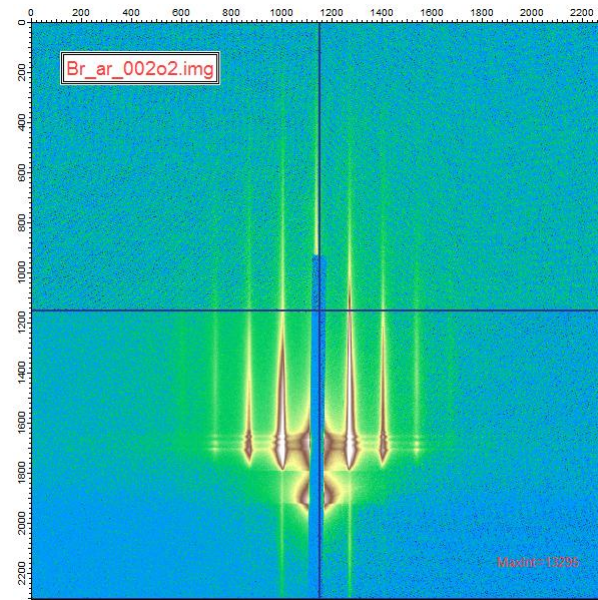
**0°**

Only **3** sec, **32409** counts!!!



**2°**

**12** sec, **13295** counts



**4°**

**50** sec, **14023**

*There must be some defects by nature.  
However, the probability is less than 2%.*

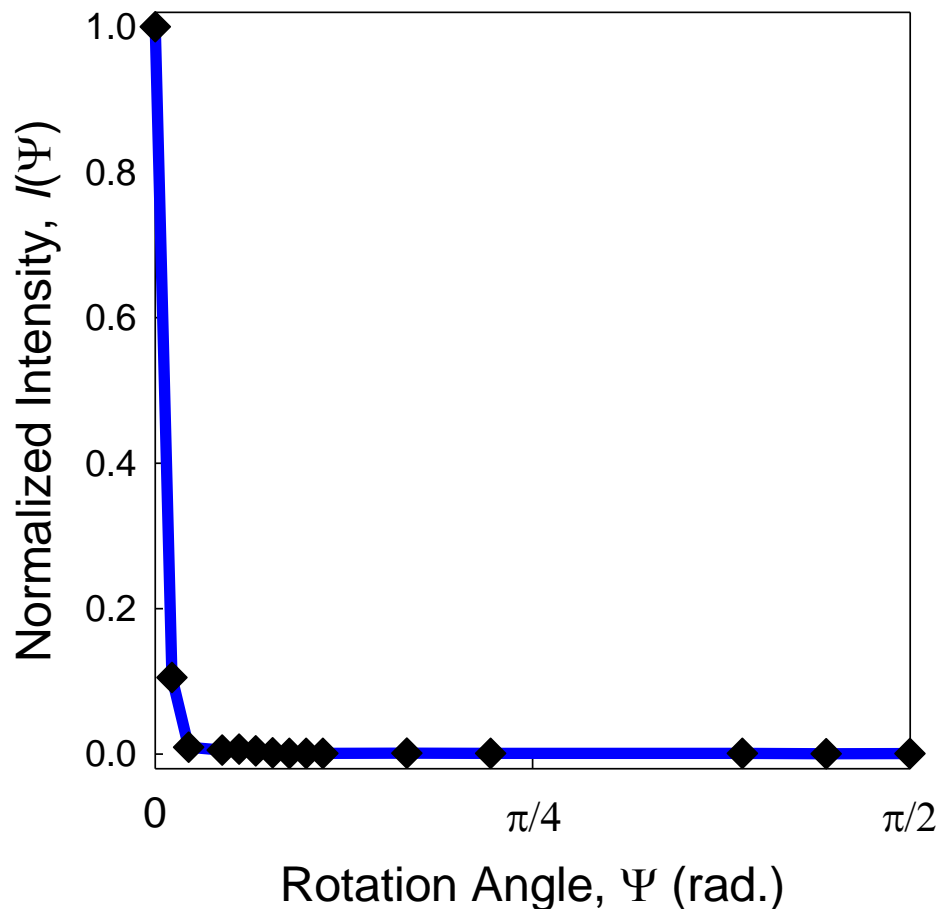
*The line pattern is **highly aligned and oriented** along one direction!*





## Orientation Parameter ( $f$ )

Intensity at (1,0) Plane



$$\begin{aligned}\langle \cos^2 \Psi \rangle &= \frac{\int I(\Psi) \cos^2 \Psi \sin \Psi d\Psi}{\int I(\Psi) \sin \Psi d\Psi} \\ &= \frac{\sum I(\Psi) \cos^2 \Psi \sin \Psi d\Psi}{\sum I(\Psi) \sin \Psi d\Psi}\end{aligned}$$

$$f = \frac{3\langle \cos^2 \Psi \rangle - 1}{2} = 0.947$$

$f$	Orientation
1	Perfectly parallel
0	Random
-0.5	Perfectly perpendicular



# *Transmission-SAXS Study: Pattern Transfer*

PBT Film

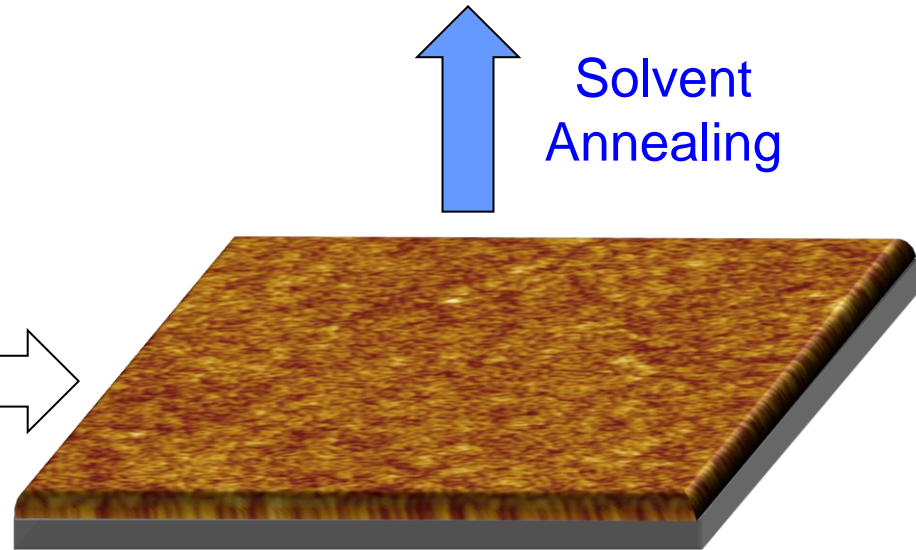
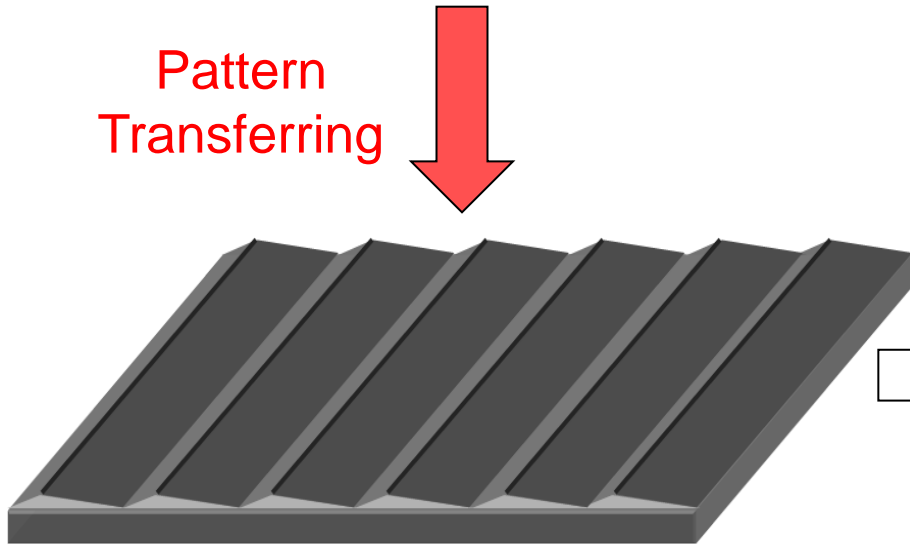
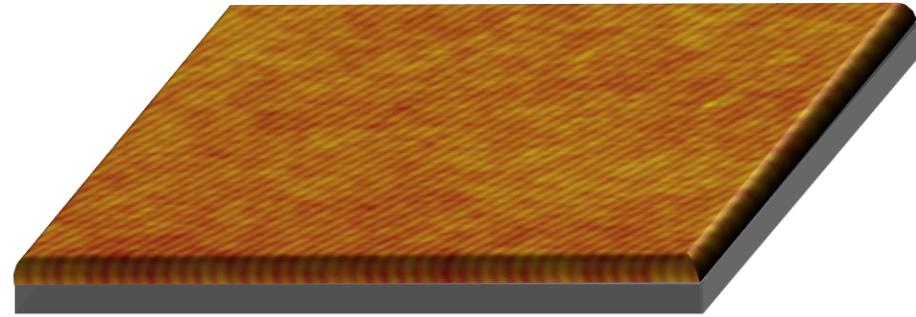
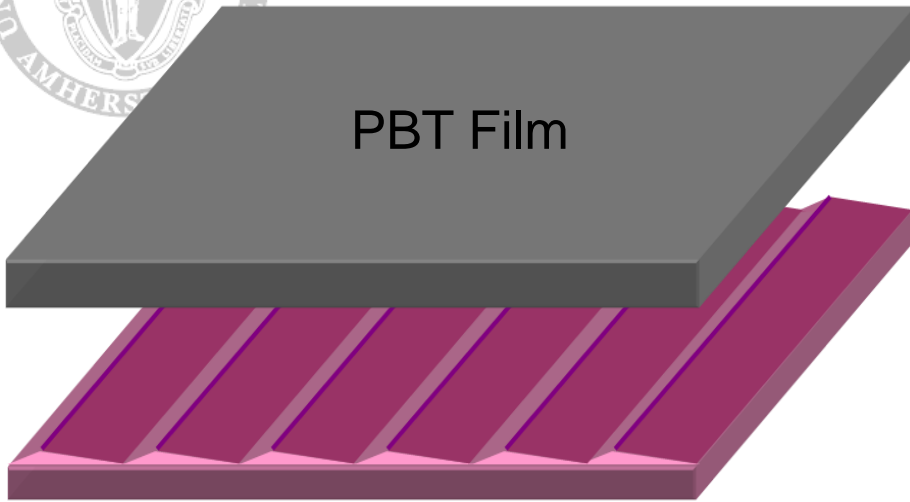
Line Patterns on Polymeric Replica

Pattern  
Transferring

Solvent  
Annealing

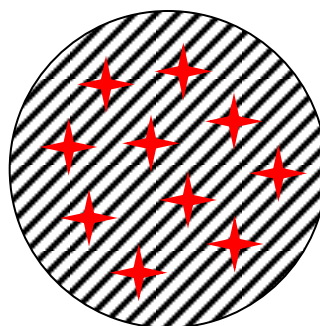
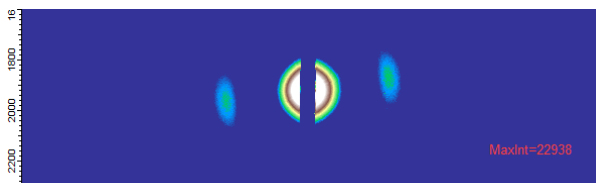
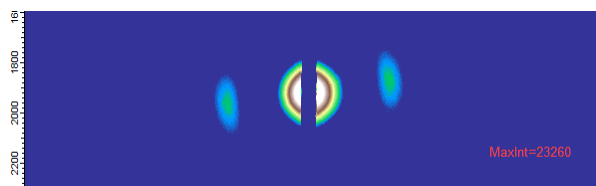
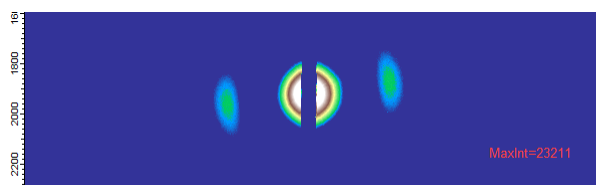
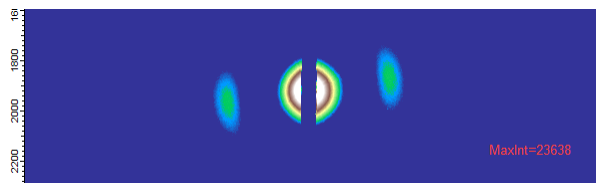
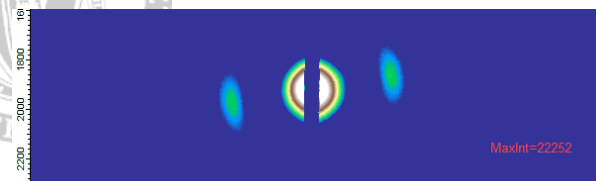
Polymeric Replica

As-spun Film on Polymeric Replica

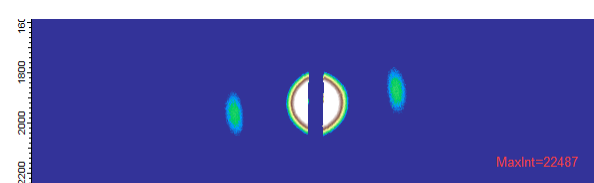
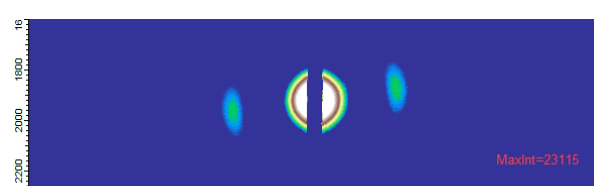
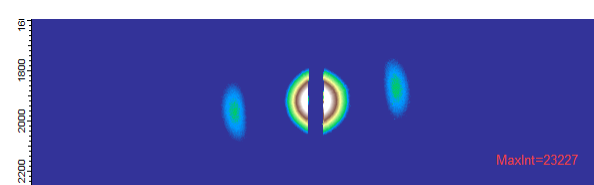
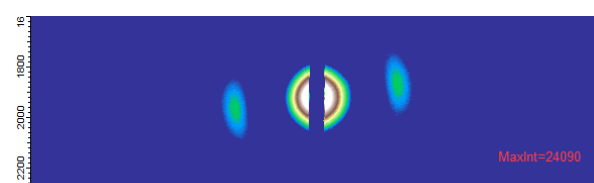
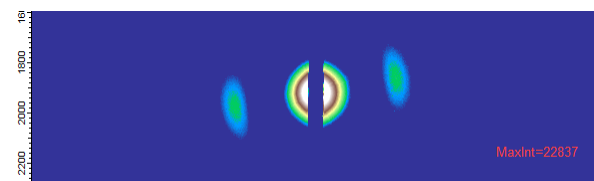




# Transmission-SAXS Study: Pattern Transfer



Peak Positions  
are same!



*The line pattern is **highly aligned and oriented** along one direction!*